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ERRATA

MOLECULAR ASSOCIATION

G. G. Longinescu

Page 389. Table 1. Known value of n for octyl methyl ether. For 20, read 30.

Page 395. Table 6. Known value of n for silver bromide. For 1, read 2.

Page 396. Formula (4) should read $A = 3.7 \left[100 - \dfrac{T}{D.\sqrt{n}} \right]$.

Page 398. The equation should read $\dfrac{T}{\sqrt{M}} + \dfrac{1000\sqrt{M}}{T} = 64$.

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The second relation should read $\dfrac{M_h}{d_h} : \dfrac{M_s}{d_s} = $ a constant.

Page 413. The formula should read $\dfrac{\gamma_1 \left(\dfrac{1000}{C_m}\right)^{\frac{2}{3}} - \gamma_2 \left(\dfrac{1000}{C_m}\right)^{\frac{2}{3}}}{t_2 - t_1} = K$.

RECENT PROGRESS IN THE MENTHONE CHEMISTRY

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INTRODUCTORY

Menthol, or "mint camphor," $C_{10}H_{20}O$, was first recognized as a crystalline principle in 1771 by the Dutch botanist Gambius, who termed it *camphora europaea menthæ piperitidis*. Its main source, the peppermint plant, which finds mention in the *Shin-J-Ho* (984) as *Megusa*, or eye herb, appears to have been cultivated in Japan for more than two thousand years. For several centuries English peppermint enjoyed a wide reputation: the oldest specimens of *Mentha piperita* now extant were collected by John Ray in 1696; they were grown in Hertfordshire, and are now in the British Museum. At the present day, although peppermint is still cultivated at Mitcham and elsewhere in England, the peppermint industry centers mainly in the United States and Japan. In America, two well-known varieties of the peppermint plant have been derived from the original English stock, namely, the black mint (*Mentha piperita vulgaris*) and the white mint (*Mentha piperita officinalis*); the former is favored for cultivation on account of its hardy nature and productivity. Japanese and Chinese peppermint oils are distilled from two varietal forms of an entirely distinct species, known respectively as *M. arvensis piperascens* and *M. arvensis glabrata* (1).

Until about 1920, only two primary substances had been used as points of departure in researches dealing with the structural chemistry and stereochemistry of the important group of homocyclic compounds centering around menthone: these substances,
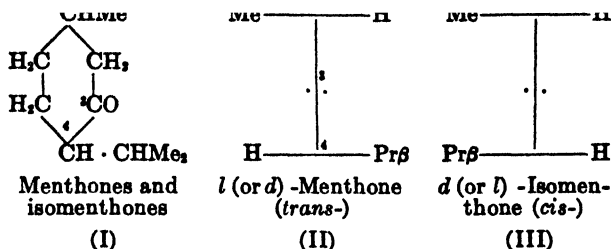
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in order of chronology as well as of importance, are menthol and thymol.

The first reference in the voluminous literature of the menthone series contains an account of an oil, $C_{10}H_{18}O$, prepared at Tokyo in 1881 by Moriya (2), who treated menthol from Japanese peppermint oil with chromic acid in a sealed tube at 120°. Although made by the oxidation of levo-rotatory menthol, the oil was optically inactive. In a note added to the paper, Prof. Atkinson made the correct suggestion that "menthol is a secondary alcohol derived from a saturated closed chain hydrocarbon formed by the addition of six atoms of hydrogen to ordinary cymene, and that the oxidation product, $C_{10}H_{18}O$, obtained by Mr. Moriya, is the corresponding ketone." Andres and Andreef (3) first succeeded in isolating menthone from peppermint oil in 1892, although it should be noted that Moriya stated in his original paper that "it is not improbable that this substance, which holds the menthol (of peppermint oil) in solution, is the same body as that formed by the action of the chromic acid liquid upon the camphor."

A certain confusion was introduced at the outset into the chemistry of menthone by Beckmann's discovery (4), in 1889, of the so-called "inversion" of the levo-rotatory ketone into a dextro-rotatory modification. *l*-Menthone, prepared by a carefully controlled oxidation of natural *l*-menthol with chromic acid mixture, had a maximum rotatory power of $[\alpha]_D$ −28.46°, and was found to be substantially identical with the levo-rotatory ketone occurring in peppermint oils. The ketone recovered from a solution in cold strong sulphuric acid showed a maximum value of $[\alpha]_D$ +28.14°, while treatment with acid or alkaline reagents, or the action of heat alone, yielded specimens with intermediate optical rotatory powers. The assumed conversion of the levo-rotatory ketone into its enantiomer, which has been repeatedly expressed or implied in the literature (5), was rendered untenable by Beckmann's further observation that the "inverted" ketone yielded an oily oxime possessing an optical rotation quite distinct from that of the crystalline and highly characteristic oxime of *l*-menthone.

The constitution (I) suggested for menthone by Semmler in 1892, and now generally accepted, indicates that the ketone should be capable of existing in *cis-* and *trans-*forms (II and III), each characterized by molecular enantiomorphism:

$$
\begin{array}{ccc}
\text{C}\cdot\text{Me} & \text{Me}\text{——————}\text{H} & \text{Me}\text{——————}\text{H} \\
\overset{\text{H}_2\text{C}\quad\text{CH}_2}{\underset{\text{H}_2\text{C}\quad\text{CO}}{\diamondsuit}} & \vdots & \vdots \\
\text{CH}\cdot\text{CHMe}_2 & \text{H}\text{——————}\text{Pr}\beta & \text{Pr}\beta\text{——————}\text{H}
\end{array}
$$

Menthones and isomenthones	*l* (or *d*) -Menthone (*trans-*)	*d* (or *l*) -Isomenthone (*cis-*)
(I)	(II)	(III)

The constitution thus provides for two ketones, menthone and isomenthone, each of which should occur in *d-* and *l-*modifications. Further, the two ketones should be interconvertible through a process of enolization, which would enable a ketone of each type to pass through a common enol-form in which the asymmetry of carbon atom (4) is temporarily annulled; since, however, carbon atom (1) remains asymmetric throughout the tautomerization, the optical activity of the molecule does not vanish in the process. The observed change of sign in the rotatory power indicates that levo-rotatory menthone passes into dextro-rotatory isomenthone, and *vice versa*. An equilibrium may thus be pictured, of the form *l*-menthone $\rightleftarrows$ *d*-isomenthone, the proportions of the two stereoisomers being determined by the particular conditions:

CH—Me $\longrightarrow$ CH—Me $\longrightarrow$ CH—Me

l (or *d*) -Menthone	*enol-l*-Menthone	*d* (or *l*) -Isomenthone
(IV)	(V)	(VI)
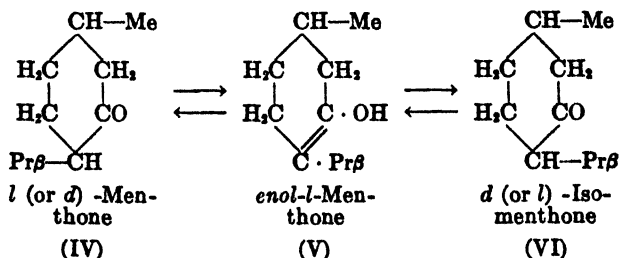
The value $[\alpha]_D$ +28.14°, observed by Beckmann, denotes therefore a definite mixture of *l*-menthone and *d*-isomenthone.

Originally there was a disposition to assign the *cis-*configuration

(III) to menthone; but according to recent observations by Zeit-
schel and Schmidt (6) this configuration should be allocated to
isomenthone, in accordance with the Auwers-Skita rule that the
higher density and refractive index are characteristic of the *cis*-
isomer. A certain amount of support for this view is provided
by Carter's measurements of parachors (7), the values for *d*- and
dl-isomenthone being somewhat higher than for *l*- and *dl*-men-
thone. Nevertheless, the evidence is not wholly convincing,
and the relative configurations of the two ketones here given can
be regarded only as provisional until accurate physical deter-
minations have been made for specimens of the active and inactive
ketones of undoubted stereochemical homogeneity.

Prominent among the early derivatives of menthone to be dis-
covered was *l*-menthylamine, first prepared by Andres and
Andreef (3), in 1892, by the reduction of *l*-menthoneoxime. A
similar method was used by Wallach (8), who also prepared a
stereoisomeric "R-menthylamine" by heating *l*-menthone with
solid ammonium formate; although dextro-rotatory, this base
was shown to be distinct from the enantiomer of *l*-menthylamine.
No other menthylamine was described until 1913, when Wallach
(9) prepared a so-called "*i*-menthylamine" by reducing *dl*-
menthoneoxime: this base has recently been shown to have
been heterogeneous, owing presumably to the occurrence of
"inversion" during the oximation of the optically inactive
ketone.

In 1912, a considerable advance in the menthone chemistry
was achieved by Pickard and Littlebury (10) as a result of their
researches on menthols. When heated with phthalic anhydride,
the menthols present in the complex mixture obtained in the
catalytic hydrogenation of thymol yielded crystalline menthyl
hydrogen phthalates. By a process of repeated fractional crys-
tallization, followed by hydrolysis, it was possible to prepare
from this product pure specimens of *dl*-menthol (m.p. 34°) and
dl-neomenthol (m.p. 51°); moreover, by treatment with appro-
priate optically active alkaloids, *dl*-menthyl hydrogen phthalate
and *dl*-neomenthyl hydrogen phthalate were resolved into
optically active components, thus yielding *d*- and *l*-menthol

(m.p. 43°) and d- and l-neomenthol (oils). Since l-menthol and d-neomenthol are oxidized by chromic acid to l-menthone, and d-menthol and l-neomenthol to d-menthone, all these menthols must be regarded as derivatives of menthone (as distinct from isomenthone).

The earlier literature of this subject contains many disconnected and conflicting references to supposed derivatives of isomenthone. Among these, a publication by Beckmann (11) in 1909 proved later to be substantially correct. The crude liquid oxime of "inverted" l-menthone furnished a supposed d-isomenthylamine hydrochloride, having $[\alpha]_D$ +17.7° in dilute aqueous solution; this material reacted with nitrous acid to yield a dextro-rotatory isomenthol, which upon oxidation passed into a ketone having $[\alpha]_D$ +93.2°.

Thus, in brief, the researches based on l-menthol and thymol had succeeded in elucidating the main chemical relationships of l- and dl-menthone, of the derived l-, d- and dl-menthols and -neomenthols, and of l-menthylamine; but while important lacunae still existed in the menthone series, the whole field of isomenthone and its derivatives awaited a systematic exploration. According to Meyer and Jacobson (12), "es wäre eine dankbare Aufgabe, die vier optisch aktiven und die beiden wahren racemischen Modificationen von krystallisirbaren Menthon-Derivaten darzustellen und unter besonderen Berücksichtigung der modernen, von van 't Hoff und Roozeboom vertretenen Anschauungen genau zu untersuchen, da dieser Fall von grundlegender Bedeutung für die Terpenchemie ist." The considerable expansion of the menthone chemistry which has occurred during the last few years is due almost entirely to the introduction into this field of work of the *Eucalyptus* ketone, piperitone.

PIPERITONE

History and occurrence

The genus *Eucalyptus*, as pointed out by R. T. Baker and H. G. Smith (13), is of immense scientific and economic importance, on account of its timbers, essential oils, exudations and dyes.

It comprises about three-quarters of the vegetation of Australia, and embraces some three hundred species, each possessing distinctive chemical characteristics. Since the examination by Cloëz (14), in 1870, of the essential oil of *E. globulus*, the presence of more than forty different components, consisting mainly of terpenes and their derivatives, has been established in *Eucalyptus* oils. The classical researches of Baker and Smith (13) have shown that the eucalypts fall broadly into three main groups, distinguished chemically by the composition of their leaf-oils and exudations (kinos) and morphologically by the leaf-venation,

TABLE 1

Characteristics of the three main groups of eucalypts

	GROUP I	GROUP II	GROUP III
Main components of leaf-oil	Pinene (bornyl acetate)	Pinene, cineole	*l*-α-Phellandrene (geranyl acetate, *l*-piperitone)
Leaf-venation	Obtuse, "feather" type	Acute, with marginal vein	Acute, "butterfly-wing" type; possibly two marginal veins
Yield of oil	To 0.5 per cent	Intermediate	To 4.5 per cent
Examples	*E. corymbosa*	*E. Smithii,* *E. globulus*	*E. amygdalina,* *E. dives,* *E. piperita*

the form and size of the cotyledons, etc. The more important characteristics which were elucidated in the course of these remarkable phytochemical researches are summarized in table 1 (15). According to Baker and Smith's evolutionary theory, the older species of the first group originated in N. W. Australia; while the third group, which predominates in S. E. Australia and Tasmania, contains the most recently evolved species.

Among the varied components of *Eucalyptus* oils, only one has been discovered which possesses ketonic properties. It imparts a strong peppermint odor to the oils of the so-called "peppermint"

eucalypts, a species of which attracted attention at Port Jackson (Sydney Harbor) soon after Governor Phillip's arrival in New South Wales, in 1788. The species is now known as *E. piperita*, or the Sydney peppermint, and the first *Eucalyptus* oil to be distilled was obtained from its leaves and used as a substitute for peppermint oil by Dr. White, Surgeon-General to the First Settlement. "The name Peppermint Tree has been given to this plant by Mr. White on account of the very great resemblance between the essential oil drawn from its leaves and that obtained from the Peppermint (*Mentha piperita*) which grows in England. This oil was found by Mr. White to be much more efficacious in removing all cholicky complaints than that of the English Peppermint, which he attributes to its being less pungent and more aromatic. A quart of the oil has been sent by him to Mr. Wilson" (16).

In 1900, the peppermint odor of this oil was shown by Smith (17) to be due to a ketone, which was not menthone as originally supposed (18); menthone, despite repeated statements to the contrary, has not been discovered in *Eucalyptus* oils. Subsequently, the new ketone, now diagnosed as $C_{10}H_{16}O$, was recognized as a new substance under the appropriate name of piperitone (13). Piperitone has since been found, apparently always in the levo-rotatory form, in twenty-three species of *Eucalyptus* (19), having the general characters indicated in the third group of table 1. The maximum amount is found in the oil of the broad-leaved peppermint (*E. dives*), which may contain from 40 to 50 per cent of the ketone, the chief remaining constituent being *l-α*-phellandrene. The yield of oil from the green leaves and twigs of *E. dives* reaches about 4 per cent, and since the regrowth from the felled or lopped trees is particularly rapid, piperitone could be produced in almost unlimited quantity upon waste land in suitable regions of Australia (as well as in other countries); it should be noted, however, that certain varietal forms of *E. dives* are practically worthless for the production of piperitone (20).

In 1921, a detailed examination of piperitone was undertaken by Read and Smith, with the later collaboration of Bentivoglio,

Hughesdon and Earl (21). During these researches, d-piperitone was discovered by Simonsen (22) in the essential oil of *Andropogon Jwarancusa*, a Himalayan grass; apparently also, it is the dextro-modification which occurs in the oils of Japanese peppermint (23) and *Cymbopogon sennaarensis* (24). It is interesting, moreover, that the pulegone of *Mentha pulegium* is replaced in *M. pulegium* var. *hirsuta* by l-piperitone (25). The ketone is also
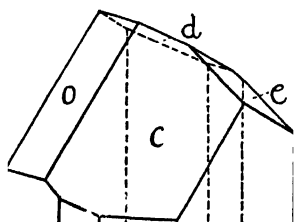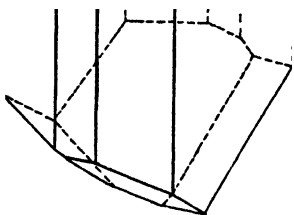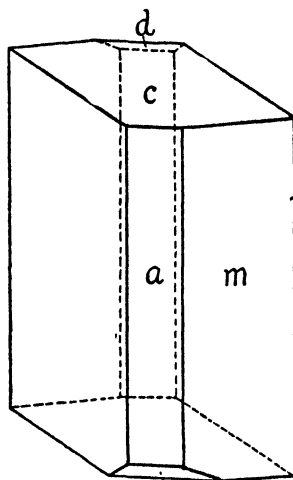
FIG. 1. *dl*-PIPERITONE-α-OXIME   FIG. 2. *dl*-PIPERITONE-β-OXIME

said to occur in camphor oil, but the sense of the optical rotation is not stated (26).

Piperitone was ultimately diagnosed as Δ^1-menthenone-3. Owing to the discovery of its ready conversion to isomenthone, the new ketone provided a fresh and extremely effective point of departure for elucidating the chemical relationships of the menthones and their derivatives, its value for this purpose being enhanced by its availability in the l-, d- and dl-modifications.

Quite apart from the novel position of piperitone in the pure chemistry of the menthone series, its ready conversion to menthol and thymol (*vide infra*) lends it a pronounced economic interest: so that, altogether, this ketone may now be claimed as one of the most important of the alicyclic compounds. For this reason the chemistry of the substance calls for treatment in some detail.

Characterization

Piperitone gives rise to a number of crystalline derivatives of exceptional beauty and distinction, prominent among which are
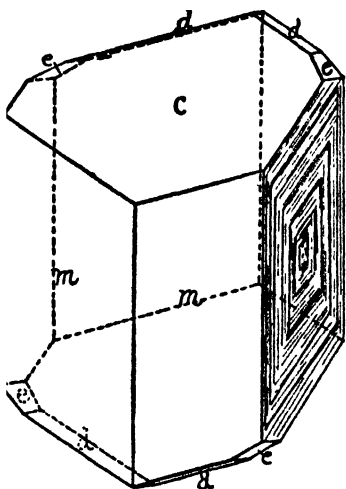
FIG. 3. BENZYLIDENE-*dl*-PIPERITONE,   FIG. 4. BENZYLIDENE-*dl*-PIPERITONE,
α-FORM   β-FORM
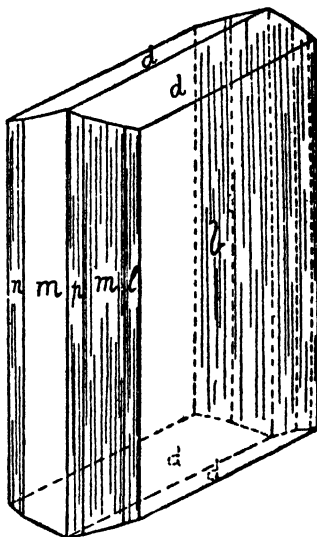
the α-oxime (m.p. 118–9°), the β-oxime (m.p. 88–9°) and the benzylidene derivative. Owing to the ease with which the active ketone racemizes, the derivatives are usually produced in the externally compensated form. The α-oxime (figure 1) and β-oxime (figure 2), which crystallize respectively in the triclinic and monoclinic systems (27), are regarded as *syn-* and *anti-*modifications. The α- and β-semicarbazones melt at 226–7° and 174–6°, respectively. The ketone also forms two hydroxylamino-oximes.

In the presence of alcoholic sodium ethoxide, piperitone condenses readily with aldehydes, giving rise to very characteristic derivatives. Benzylidene-*dl*-piperitone (28) provides a remarkable example of enantiotropic dimorphism: the monoclinic, pale yellow α-form (figure 3) melts at 59–61°, and the rhombic, deeper yellow β-form (figure 4) melts at 63–4°. The α-form is the stable modification at the ordinary temperature, but each form is readily procurable in a state of complete freedom from the other. For diagnostic purposes, the preparation of anisylidene-*dl*-piperi-
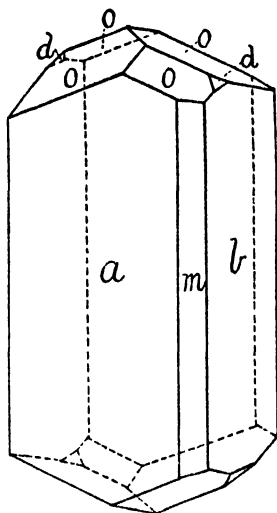
FIG. 5. ANISYLIDENE-*dl*-PIPERITONE

tone (m.p. 98°) is to be recommended (29); it forms pale yellow rhombic prisms (figure 5), and does not display dimorphism. It is also useful to note that the oximes are readily soluble in dilute mineral acids, from which they may be recovered by the addition of ammonia. This behavior differentiates piperitone from several closely related ketones.

Piperitone may be extracted from essential oils by means of hot aqueous solutions of sodium bisulfite or normal sulfite (30), but partial racemization invariably attends its liberation from the crystalline bisulfite compound. Racemization occurs also when

the active ketone is maintained at 200°, distilled under atmospheric pressure, or treated with alcoholic sodium ethoxide (31). Fractional distillation of a piperitone-bearing oil under ordinary pressure yields the optically inactive ketone. Thus the only method which can be used to isolate specimens possessing the maximum rotatory powers of about $[\alpha]_D^{20}$ ±50° is that of repeated fractional distillation under diminished pressure; products isolated in this way appear to contain some dl-piperitone (32), in addition to small quantities of other impurities (31). The active forms of the ketone are also difficult to characterize chemically: from l-piperitone a viscid oxime, having $[\alpha]_D$ +238° in benzene, has been prepared (31).

Pure dl-piperitone, prepared through the bisulfite compound and the α-semicarbazone, had the following physical constants (33): b.p. 113° at 18 mm., 232–233° at 768.6 mm., d_4^{20} 0.9331, n_D^{20} 1.4845, $[R_L]_D$ 46.70. The calculated molecular refractivity for a ketone, $C_{10}H_{16}O$, with one double bond is 45.82, so that the exaltation is 0.88 unit. It is interesting that the observed value is almost identical with the value (46.76) calculated for an enolic form.
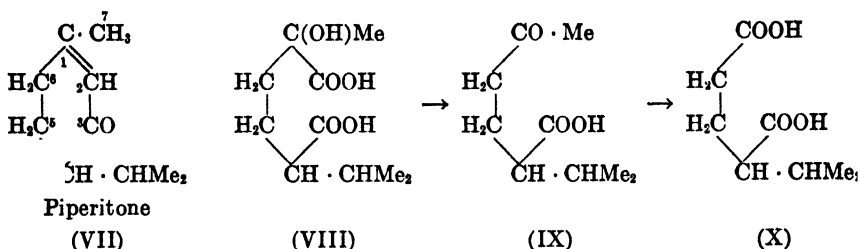
Constitution

The chemical identity of the ketone from the various sources which have been enumerated was inferred from a study of the oximes and other characteristic derivatives. In this way, a complete goniometric correspondence was established (27) between specimens of the dl-α-oxime prepared from the oils of E. dives (Australia) and A. Jwarancusa (India). Since he was able to reduce piperitone to dl-menthol and oxidize it to thymol, Smith (13) recognized the substance as a menthenone-3. The disruptive oxidation of the ketone from Japanese peppermint oil (23) had yielded α-hydroxy-α-methyl-α'-isopropyladipic acid (VIII), γ-acetyl-α-isopropylbutyric acid (IX) and α-isopropylglutaric acid (X), and closely similar results were obtained by Simonsen (22), using the Indian ketone. Thus, assuming (a) the chemical identity of the ketone from the various sources, and (b)

the absence of molecular rearrangement prior to oxidation, piperitone would be Δ¹-menthenone-3 (VII), a ketone which had been synthesized from 1,3,4-trihydroxymenthane and briefly described by Wallach (34) in 1908:

$$
\begin{array}{cccc}
\overset{7}{\text{C}}\cdot\overset{7}{\text{CH}}_3 & \text{C(OH)Me} & \text{CO}\cdot\text{Me} & \text{COOH} \\
\text{H}_2\text{C}^6\quad_2\text{CH} & \text{H}_2\text{C}\quad\text{COOH} & \text{H}_2\text{C}\quad & \text{H}_2\text{C} \\
\text{H}_2\text{C}^5\quad_3\text{CO} & \text{H}_2\text{C}\quad\text{COOH} & \text{H}_2\text{C}\quad\text{COOH} & \text{H}_2\text{C}\quad\text{COOH} \\
\text{3H}\cdot\text{CHMe}_2 & \text{CH}\cdot\text{CHMe}_2 & \text{CH}\cdot\text{CHMe}_2 & \text{CH}\cdot\text{CHMe}_2 \\
\text{Piperitone} & & & \\
\text{(VII)} & \text{(VIII)} & \text{(IX)} & \text{(X)}
\end{array}
$$

This conclusion concerning the constitution of piperitone was confirmed by Read, Smith and Hughesdon (35), by means of a method which utilized only mild reagents at the ordinary temperature and avoided any disruption of the ring. If dl-piperitone has the constitution (VII), it is apparent that condensation with benzaldehyde cannot occur in position (2); whereas if the double bond is in any position except Δ¹, condensation will be confined to position (2). The latter condition will also apply to the ketone obtained upon hydrogenating dl-piperitone. The following two series of operations were accordingly carried out: (i) dl-piperitone → benzylidene-dl-piperitone → benzyl-dl-isomenthone; (ii) dl-piperitone → dl-isomenthone → 2-benzylidene-dl-isomenthone → 2-benzyl-dl-isomenthone. Since the two final products were distinct, piperitone is evidently the Δ¹-ketone.

Simonsen (22), suggested that condensation with aldehydes occurs in position (6), owing to the activation exerted by the adjacent ethylenic linkage; a similar activation had indeed been observed by Wallach (36) in the case of Δ⁴-menthenone-3, which forms a 2,6-dibenzylidene derivative (XI). Later, however, it was shown by Earl and Read (29) (37) that benzylidene-dl-piperitone yields α-isopropylglutaric acid (X), and not isopropylsuccinic acid, when oxidized with potassium permanganate in cold acetone. It may therefore be concluded that condensation with aldehydes occurs in the 7-position, the system C:C·CO,

curiously enough, exerting its maximum activating effect in the side-chain rather than in the ring:

2, 6-Dibenzylidene-Δ⁴-menthenone-3
(XI)

7-Benzylidene-piperitone
(XII)
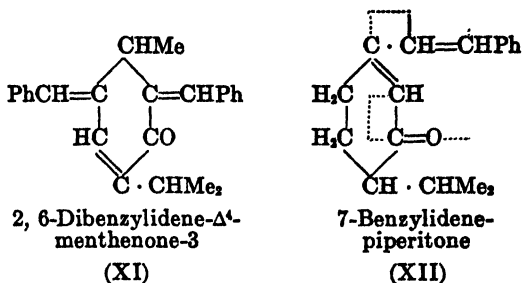
In this instance there is no tendency to form a dibenzylidene derivative. It is of interest that the duplicated conjugation presented by the molecule of benzylidenepiperitone, and indicated in formula (XII), is often associated with dimorphism (38).

That piperitone is an $\alpha\beta$-unsaturated ketone is supported by the fact that its molecular refractivity displays the exaltation characteristic of menthenones of this type (39); moreover, it forms a hydroxylamino-oxime, and when reduced with sodium amalgam in aqueous alcohol gives rise to a so-called "bimolecular ketone" (13), characterized by Carter and Read (40) as 1,1'-bismenthone:

1, 1'-Bismenthone
(XIII)
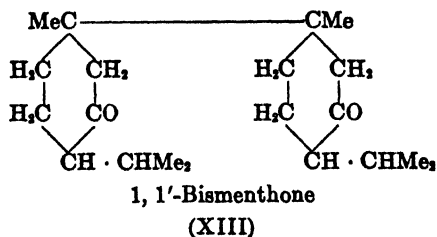
This derivative, the formation of which is very characteristic of piperitone, exists in two externally compensated forms, m.p. 166–7° and 135–6°.

As an $\alpha\beta$-unsaturated ketone, piperitone resembles other important components of essential oils, including pulegone, verbenone, carvotanacetone and carvone:

CMe
H₂C CH
H₂C CO
CH
CHMe₂
Piperitone
(XIV)

CHMe
H₂C CH₂
H₂C CO
C
CMe₂
Pulegone
(XV)

CMe
HC CH
CMe₂
H₂C CO
CH
Verbenone
(XVI)

CMe
HC CO
H₂C CH₂
CH
CHMe₂
Carvotan-acetone
(XVII)
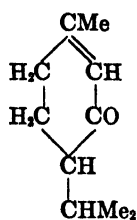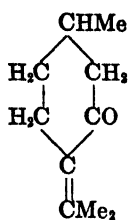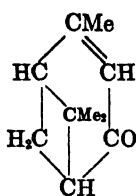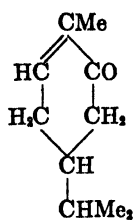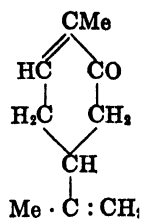
CMe
HC CO
H₂C CH₂
CH
Me · C : CH₂
Carvone
(XVIII)

Non-conjugated structures, such as those presented by isopulegone and dihydrocarvone, are also found in natural ketones of this class; but in such instances there is always a tendency towards isomerization into the more stable conjugated form. Although *Eucalyptus* piperitone is usually regarded as chemically homogeneous, recent work (41) has indicated the possibility of the presence in it of an intra-annular tautomeride of Δ^1-menthenone-3, such as the Δ^6-ketone; this would be related to the Δ^1-compound in much the same way as isopulegone to pulegone:

CHMe
H₂C CO
H₂C CH₂
CH
Me · C : CH₂
Dihydrocarvone
(XIX)

CHMe
H₂C CH₂
H₂C CO
CH
Me · C : CH₂
Isopulegone
(XX)
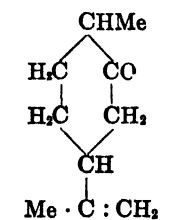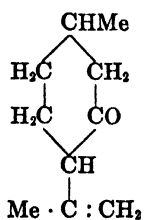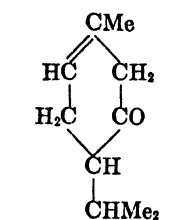
CMe
HC CH₂
H₂C CO
CH
CHMe₂
Δ^6-Menthenone-3
(XXI)

Racemization

As already stated, the optically active forms of piperitone readily undergo racemization when submitted to the action of heat or alkaline reagents; the racemizing action of acid reagents is less marked (31). This behavior has been attributed to enolization, since this process annuls the asymmetry of the molecule:

keto-Piperitone   enol-Piperitone
(XXII)   (XXIII)
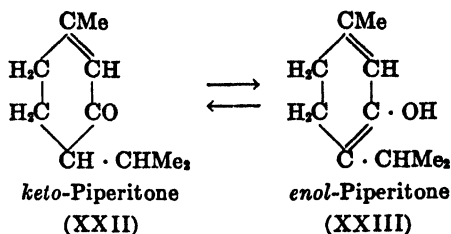
It is evident that the racemization of piperitone is analogous to the "inversion" of *l*-menthone (formulae IV, V and VI); in the latter process, however, the molecule retains its optical activity owing to the undisturbed asymmetry of carbon atom (1), which in piperitone is symmetric.

Oxidation

The disruptive oxidation of piperitone has been reviewed in the discussion of its constitution; economically, however, the main interest centers around milder oxidative processes which leave the ring intact. Piperitone may be converted to thymol in various ways, notably by oxidation with ferric chloride in glacial acetic acid (42), by treatment with halogens (43), or by dehydrogenation (43). Oxidation with permanganate yields a small proportion of diosphenol (24), and the ketone reacts with hypochlorous acid to form a crystalline chlorohydrin, m.p. 101–2° (43).

Reduction

When reduced with sodium amalgam in moist ether or aqueous alcohol, piperitone affords a mixture of 1,1'-bismenthone, *dl*-isomenthol and *dl*-menthol (*vide infra*); the yield of menthol is increased by using absolute alcohol (24) (42). According to Smith and Penfold (42), the ketone is converted to *dl*-menthone when hydrogenated in the presence of nickel at 180°, but the product also contains *dl*-isomenthone (*vide infra*). Piperitone has been utilized successfully as a commercial source of *dl*-menthol and also of thymol.

During reduction by any of the above processes, optically active piperitone undergoes a preliminary racemization, and thus

gives rise to externally compensated menthones and menthols. In 1922, however, it was shown by Hughesdon, Smith and Read (44) that when hydrogenated according to Skita's method, *l*-piperitone yielded a highly dextro-rotatory product containing *d*-isomenthone. Most of the recent advances in the chemistry of the stereoisomeric menthones, menthols and menthylamines, which will now be discussed, followed from this discovery.

THE APPLICATION OF PIPERITONE IN THE MENTHONE CHEMISTRY

The menthones

In contact with an aqueous medium containing colloidal palladium, preferably at temperatures between 35° and 20°, *l*-piperitone readily absorbs a molecular proportion of hydrogen and gives rise to an optically active mixture of menthones of reversed and enhanced rotatory power. Thus, in the original experiments (45), a specimen of *l*-piperitone having $[\alpha]_D - 51.5°$ afforded a menthone with $[\alpha]_D + 65.1°$. That this product was not *d*-menthone was apparent from its high rotatory power, the maximum value for *l*-menthone recorded by Beckmann (4) being $[\alpha]_D - 28.46°$; since, in addition, the product showed a rapid decline in rotatory power when brought into contact with alkali, it was diagnosed as consisting essentially of *d*-isomenthone. This conclusion was confirmed by Read and Robertson (32), who showed that when submitted to the action of heat, alkaline reagents, etc., the hydrogenated product gave equilibrium mixtures of *d*-isomenthone and *l*-menthone closely similar to the mixtures afforded by *l*-menthone under similar conditions. The equilibrium proportions of *d*-isomenthone formed through the action of alcoholic sodium ethoxide, heat (200°) and melting 90 per cent sulphuric acid upon pure *l*-menthone were later found to be about 30, 37 and 46 per cent, respectively (46). By hydrogenating *d*-piperitone, from the oil of *Andropogon Jwarancusa*, a corresponding product composed mainly of *l*-isomenthone was obtained: this was converted by enolizing agents to mixtures of *l*-isomenthone and *d*-menthone. Thus, the "inversion" of *l*-menthone, originally observed by Beckmann (4),

represents one phase of a reversible process of the type: l (or d)-menthone $\rightleftarrows$ d (or l)-isomenthone.

In order to prepare optically pure d-isomenthone, hydrogenated l-piperitone was converted to d-isomenthol in the way described below; when carefully oxidized with chromic acid mixture, which was found to exercise only a slight "inverting" action under the conditions adopted, this substance yielded d-isomenthone having $[\alpha]_D^{15}$ $+$ 91.7° (46). Since the highest value yet observed for l-menthone is $[\alpha]_D^{20}$ $-$ 29.6° (32), Beckmann's "inverted" l-menthone, with the maximum value $[\alpha]_D$ $+$ 28.14°, presumably contained about 52 per cent of l-menthone and 48 per cent of d-isomenthone. l-Menthone predominates in all the equilibrated mixtures yet examined, but so far a literal inversion of the rotatory power of d-isomenthone has not been observed. Specimens of optically pure isomenthones are difficult to prepare, owing to the sensitiveness of these substances to heat and other enolizing influences; the ketones are also difficult to characterize. d-Isomenthoneoxime is a colorless, viscid oil, having n_D^{17} 1.4830 and $[\alpha]_D^{15}$ $+$ 45.1° in absolute alcohol; the most characteristic derivative yet prepared is the oxime hydrochloride, which forms large transparent prisms, m.p. 132°, $[\alpha]_D^{15}$ $+$ 38.6° in chloroform (46). A study of the relationships existing between l-menthone and d-isomenthone indicates (a) that the optical rotatory effect of carbon atom (1) is less than that of (4), and (b) that the optical effects of these two centers of asymmetry are opposed in the active menthones and conjoined in the active isomenthones.

dl-Isomenthone contaminated with dl-menthone has been prepared by hydrogenating dl-piperitone and also by oxidizing the mixture of menthols obtained when dl-piperitone is reduced with sodium and alcohol (47); it yields a characteristic oxime, which forms anorthic crystals (figure 6), m.p. 99–100°. The α-semicarbazone melts at 219–20°. The pure ketone could obviously be prepared by oxidizing dl-isomenthol (*vide infra*), but this has not yet been done. The "inactive menthone" prepared by Wallach (36) by hydrogenating synthetic dl-Δ^1-menthenone-3 was evidently a mixture of dl-menthone and dl-isomenthone (47), and the same statement applies to the product formed in the

hydrogenation of piperitone in the presence of nickel at 180° (42).
Thus, *l*-piperitone with $[\alpha]_D$ − 22.0°, when hydrogenated in this
way, gave a product having $[\alpha]_D$ + 11.0° (1-dcm. tube), containing
dl- and *d*-isomenthone and *dl*- and *l*-menthone (45).

It is interesting to note that neither *dl*-menthone nor *dl*-
isomenthone can be obtained in any ordinary way by racemizing
optically active menthones. In this respect the menthones differ
markedly from the piperitones. Although the latter readily
suffer racemization, once an optically active piperitone has been
hydrogenated by Skita's method the optical activity cannot be
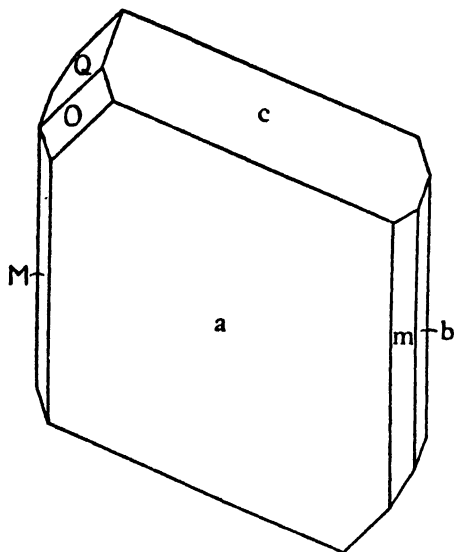
FIG. 6. *dl*-ISOMENTHONEOXIME

annulled. The exceptional value of piperitone in the menthone
chemistry is largely bound up with the circumstance that it is
available in the *l*-, *d*- and *dl*-forms, each of which leads directly
to the corresponding forms of isomenthone and menthone.

Much interesting work remains to be carried out with stereo-
chemically pure specimens of the active and externally compen-
sated forms of menthone and isomenthone. Notably, the accu-
rate determination of physical data for the various ketones should

aid materially in settling the question of their relative molecular configurations. Moreover, *d*-menthone, which has hitherto been a very rare substance, has lately been rendered accessible from *dl*-piperitone by way of *dl*-menthylamine and *d*-menthol, as described below.

Hydrogenation of menthenones

The striking effect of hydrogenating piperitone rendered it of interest to apply Skita's method to other optically active menthenones, particularly as Skita and Ritter (48) had stated that *d*-pulegone when treated in this way had yielded a "partly racemized *d*-menthone." Table 2 (32) contains a summary of the results obtained upon hydrogenating the purest available

TABLE 2

Results obtained by hydrogenation of some optically active menthenones

MENTHENONE	$[\alpha]_D^{15}$ OF MENTHENONE	$[\alpha]_D^{15}$ OF DERIVED MIXTURE OF MENTHONES	PERCENTAGE OF ISOMENTHONE
d-Pulegone	+23 6°	+33.5°	52
l-Δ⁴-Menthenone-3	−78 4	+43 2	60
l-Piperitone	−53 9	+69.1	81–75
d-Piperitone	+62 5	−71.4	83–78

specimens of *d*-pulegone, *l*-Δ⁴-menthenone-3, *l*-piperitone and *d*-piperitone. The second of these ketones was prepared from *l*-menthol through the methyl ester of *l*-menthylxanthic acid, by Tschugaev's method (49), and *d*-pulegone was isolated from French oil of pennyroyal (*Mentha pulegium*).

The results of equilibration experiments showed that the first two products consisted of mixtures of *d*-isomenthone and *l*-menthone. Hence it is clear that the spatial environment of the sole asymmetric carbon atom (1) of *d*-pulegone, as also of *l*-Δ⁴-menthenone-3, is analogous to that of the corresponding asymmetric carbon atom (1) of *l*-menthone or *d*-isomenthone. This being so, the creation of the second asymmetric carbon atom (4), which occurs during the hydrogenation, leads necessarily to a mixture of *l*-menthone and *d*-isomenthone, i.e. to two substances

differing only in the asymmetry of carbon atom (4). In these instances, the qualitative composition of the products would not be affected by the occurrence of enolization during the hydrogenation. From the rotatory powers of the products from these two menthenones it is seen that they contain only a slight preponderance of d-isomenthone over l-menthone.

CME	CHMe	CHMe	CMe

$$H_2C \quad CH_2 \qquad H_2C \quad CH_2 \qquad H_2C \quad CH_2 \qquad H_2C \quad CH$$

$$H_2C \quad CO \qquad H_2C \quad CO \qquad HC \quad CO \qquad H_2C \quad CO$$

$$CH \cdot CHMe_2 \qquad C : CMe_2 \qquad C \cdot CHMe_2 \qquad CH \cdot CHMe_2$$

Menthone	Pulegone	Δ⁴-Menthenone-3	Piperitone
(XXIV)	(XXV)	(XXVI)	(XXVII)
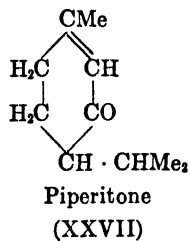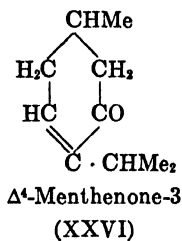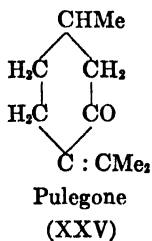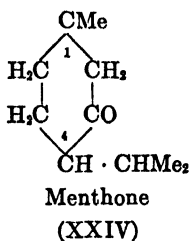
Similarly, the spatial environment of the sole asymmetric carbon atom (4) of l-piperitone is analogous to that of the corresponding asymmetric carbon atom (4) of d-isomenthone, which forms the main product of hydrogenation of the *Eucalyptus* ketone. The creation of the second asymmetric carbon atom (1) in the hydrogenation process should therefore lead to a mixture of d-isomenthone and d-menthone, since these two substances differ only in the asymmetry of carbon atom (1). The presence of dl-isomenthone in the hydrogenation product of l-piperitone (45) must be ascribed to the presence of dl-piperitone in the original ketone or to its partial racemization during the process of hydrogenation. In the latter event, simultaneous enolization of d-isomenthone would lead to the formation of some l-menthone. It is therefore likely that the hydrogenation product of l-piperitone contains dl-isomenthone, dl-menthone and l-menthone associated with the main product, d-isomenthone. The results of equilibration experiments (32) indicate that the contamination consists largely of l-menthone, produced by enolization during the hydrogenation. Assuming the product to consist wholly of d-isomenthone and l-menthone, the observed rotatory power corresponds to the presence of 81 per cent of the former substance; this proportion falls to 75 per cent if the product is considered

as a mixture of *d*-isomenthone with *dl*-isomenthone and *dl*-menthone. A slightly higher proportion of *l*-isomenthone was found in the hydrogenation product of *d*-piperitone, as shown in table 2.

On comparing the two types of hydrogenation, it is apparent that the stereochemical effect of asymmetric center (4) upon the additive process is much greater than that of asymmetric center (1). In practice, it was found that the hydrogenation occurred more rapidly with piperitone than with the other ketones. Of the four ketones under consideration, *d*-piperitone provides the only practical source of *d*-menthone by direct hydrogenation.

Upon treatment with alcoholic sodium ethoxide, the crude hydrogenation products of *l*-, *d*- and *dl*-piperitone yield mixtures containing a maximum proportion of about 70 per cent of *l*-, *d*- or *dl*-menthone, respectively, and this appears to be the highest proportion of menthone (as distinct from isomenthone) which piperitone can yield by a direct process. In no case has a pure isomenthone been obtained by the direct hydrogenation of a menthenone; the pure *d*-, *l*- and *dl*- forms of this ketone are at present accessible only by oxidizing the corresponding isomenthols, prepared as outlined below.

The menthylamines

The menthylamine constitution (XXVIII), since it includes three dissimilar asymmetric carbon atoms (1,3,4), demands the existence of eight optically active stereoisomers, together with four externally compensated forms. Two of these pairs of active forms will be derived from menthone (II above) and the remaining two pairs from isomenthone (III). Their nomenclature may be conveniently based upon the system devised by Aschan (50) and adopted by Pickard and Littlebury (10): the names are thus menthylamine, neomenthylamine, isomenthylamine and neo-isomenthylamine. A corresponding nomenclature applies to the four pairs of optically active menthols (*vide infra*). The spatial relationships are appropriately represented by the use of projection formulas:
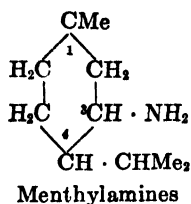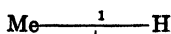
Menthylamines	Projection nucleus for menthylamines and menthols	Projection nucleus for isomenthylamines and isomenthols
(XXVIII)	(XXIX)	(XXX)
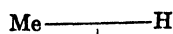
Prior to the work under review, only two of the twelve possible menthylamines had been prepared in a state of purity: these, as pointed out in the introductory section, were *l*-menthylamine, prepared by reducing *l*-menthoneoxime, and Wallach's "R-menthylamine" obtained (together with *l*-menthylamine) by heating *l*-menthone with ammonium formate (8). Although the second base is dextro-rotatory, it is not the enantiomer of *l*-menthylamine. Later, Wallach (51) showed that while *l*-menthylamine reacted with nitrous acid to yield *l*-menthol, the same reaction when applied to "R-menthylamine" furnished large quantities of a menthene having $[\alpha]_D + 55.44°$. In the latter case the preliminary formation of a menthol was obviously followed by the elimination of water, and Wallach concluded that the groups —NH₂ (3) and —OH (4) occupy *cis*- and *trans*-configurative positions, respectively, in the molecules of "R-menthylamine" and *l*-menthylamine. From its mode of formation and its ready conversion to *l*-menthol, the latter substance is obviously derived from *l*-menthone; but whether "R-menthylamine" was to be regarded as a menthylamine or an isomenthylamine remained unsettled.

A fuller study of the reactions between these two bases and nitrous acid (32) (52) has shown that *l*-menthylamine yields *l*-menthol associated with a smaller amount of partly racemized *d*-Δ³-menthene, and that although "R-menthylamine" furnishes the latter substance as the main product, a small proportion of *l*-menthol is also formed. It follows that these two bases are menthone derivatives, to which, accepting Wallach's conception, may be assigned the following relative molecular configurations:

$$Me-\!\!\!\stackrel{1}{\underset{|}{}}\!\!\!-H \qquad\qquad Me-\!\!\!\underset{|}{}\!\!\!-H$$

$$H-\!\!\!\stackrel{2}{\underset{|}{}}\!\!\!-NH_2 \qquad\qquad NH_2-\!\!\!\underset{|}{}\!\!\!-H$$

$$H-\!\!\!\stackrel{4}{}\!\!\!-Pr\beta \qquad\qquad H-\!\!\!\underset{|}{}\!\!\!-Pr\beta$$

l (or d)- d (or l)-Neo-
Menthylamine   menthylamine
(XXXI)   (XXXII)
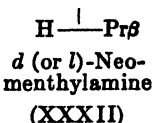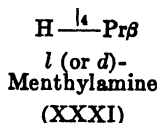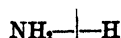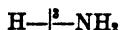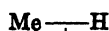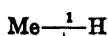
"R-menthylamine" thus becomes d-neomenthylamine, and it may be prepared (through the crystalline formyl derivative) by heating l-menthone, d-isomenthone, or any mixture of these two ketones, with ammonium formate. Similarly, l-neomenthylamine (32) and dl-neomenthylamine (53) have been made from the hydrogenation products of d-piperitone and dl-piperitone, respectively. l-Neomenthylamine is more easily prepared by the optical resolution of dl-neomenthylamine with d-tartaric acid (54).

The neomenthylamines form hydrochlorides which melt below 200° and dissolve in light petroleum, and differ thereby from the other three families of menthylamines; in addition, they are distinguished by the beauty of their crystalline derivatives. The crystals of dl-neomenthylamine hydrochloride (figure 7) are monoclinic and show no resemblance to those of the d-component (figure 8), which are also monoclinic; the externally compensated substance is therefore truly racemic. Formyl-dl-neomenthylamine (figure 9) and formyl-d-neomenthylamine (figure 10) offer an exceptional crystallographic relationship: the crystals are orthorhombic and closely related; but while those of the d-component are holohedral, solutions of the dl-compound deposit right- and left-handed hemihedral crystals which display a faint optical activity in alcohol. In this interesting case the crystallographic differentiation of d- and l-forms appears to be facilitated by the presence in the solution of the opposite kind of molecule (55).

The oxime prepared from l-menthone in a faintly acid medium at the ordinary temperature is homogeneous, and when reduced it yields practically pure l-menthylamine (32). The best experi-

mental conditions for the production of pure *l*-menthylamine having been established under polarimetric control, similar processes were applied in preparing pure *dl*-menthylamine: the principle of preliminary exploration with the aid of the polarimeter, which is here manifest, was adopted repeatedly in the

FIG. 7. *dl*-NEOMENTHYLAMINE HYDROCHLORIDE
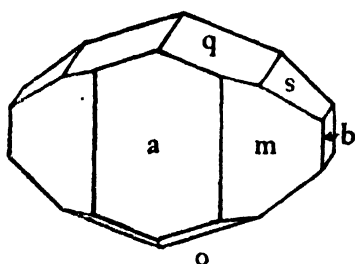
FIG. 8. *d*-NEOMENTHYLAMINE HYDROCHLORIDE
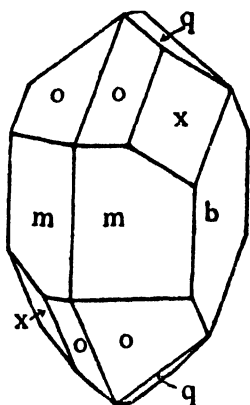
FIG. 9. FORMYL-*dl*-NEOMENTHYLAMINE   FIG. 10. FORMYL-*d*-NEOMENTHYLAMINE
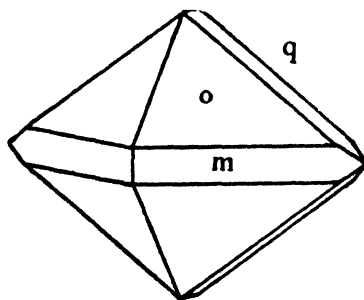
course of these investigations on menthones, menthols and menthylamines. *dl*-Menthylamine (table 3) is readily accessible from *dl*-menthol, through *dl*-menthone and *dl*-menthoneoxime; it reacts with nitrous acid to yield *dl*-menthol and some *dl*-Δ³-menthene (53). It is apparent that *d*-menthylamine might be prepared from *d*-piperitone by way of *d*-menthone, but the best

practical approach to this valuable optically active base lies through *dl*-menthylamine: it has recently been shown that when *dl*-menthylamine is crystallized with *d*-tartaric acid the less soluble of the two diastereoisomeric acid salts is of the form *dAd*B. Pure *d*-menthylamine has therefore been prepared in this way (54).

The hydrogenation product of *l*-piperitone, consisting mainly of *d*-isomenthone, furnished a viscid liquid oxime, from which

TABLE 8

Preparation of certain stereoisomeric menthylamines, etc.

		dl-Menthone† (pure), etc.	
		↑	
l-Menthol		*dl*-Menthol† (table 11)	
↑		↑	
l-Menthyl- amine†	← Formyl-*l*-men- thylamine	*l*-PIPERITONE*†	
↑	↑	↓	
l-Menthone- oxime†	← *l*-Menthone*† ⇄	*d*-Isomenthone*†	→ *d*-Neoisomen- thylamine
	↓	↓	
	Formyl-*d*-neo- menthyl- amine*†	*d*-Isomenthoneoxime*†	
	↓	↓	
	d-Neomenthyl- amine†	*d*-Isomenthylamine*†	
	↓	↓	
	d-Δ³-Menthene [+*l*-Menthol]†	*d*-Isomenthol [+ *d*-Δ³- Men- thene]*†	

d-Isomenthone (pure)
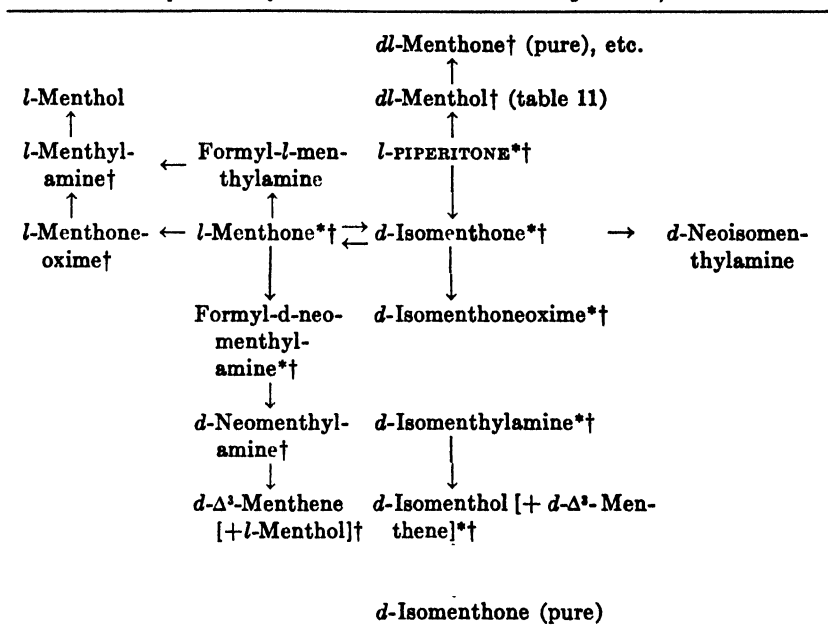
upon reduction with sodium and alcohol a new dextro-rotatory menthylamine was readily isolated (32). From the method of preparation, this base was regarded as *d*-isomenthylamine; its configurational resemblance to *l*-menthylamine was confirmed by the observation (46) that in reaction with nitrous acid it yielded *d*-isomenthol, together with partly racemized *d*-Δ³-menthene, in the approximate ratio 2:1. By similar processes, *l*-

and *dl*-isomenthylamine were prepared from *d*- and *dl*-piperitone, respectively (32) (53).

The chief processes concerned in the preparation of the stereo-isomeric menthylamines are summarized in table 3. The operations marked with an asterisk have been accomplished with both enantiomorphous forms of the substances concerned, and those in which the externally compensated substances also have been used are marked with a dagger.

In searching for the remaining group of neoisomenthylamines, it appeared that since *l*-menthone and *d*-isomenthone undergo

TABLE 4

Important derivatives of four menthylamines

DERIVATIVE		MENTHYLAMINES			
		l-	*d*-Neo-	*d*-Iso-	*d*-Neoiso-
Hydrochloride............	m. p.	>280°	189°	>250°	>250°
	$[\alpha]_D$	−36 6°	+21 5°	+23 6°	+20 9°
Formyl.............	m. p.	102–103	117–118	45–46	Liquid
	$[\alpha]_D$	−83 8	+53 8	+31 3	−3.9
Acetyl...................	m. p.	145	169–170	77–79	99–100
	$[\alpha]_D$	−81 7	+53 0	+30 7	−2 6
Benzoyl................	m. p.	157	121 5	97–98	151
	$[\alpha]_D$	−62 8	+22.7	+18 3	−10.4
Benzylidene....	m. p.	69–70	45–46	67–68	68–69
	$[\alpha]_D$	−132 5	+61 7	+90.7	−34 2
Salicylidene.	m. p.	57–58	99–100	122	99–100
.	$[\alpha]_D$	−119.2	+30 0	+77.6	−17.9

"inversion" when heated with ammonium formate, the product should contain the iso-analogues of *l*-menthylamine and *d*-neomenthylamine. A study of the derivatives of *l*-, *d*-neo- and *d*-iso-menthylamine eventually led to an investigation of the mixture of salicylidene derivatives furnished by this product. *d*-Neoisomenthylamine, which was isolated as an outcome of this work (52), is a feebly dextro-rotatory base; but its derivatives, apart from the salts, are mainly levo-rotatory. The *l*-form of this base could be prepared from *d*-piperitone, but the isolation of the *dl*-base has so far proved impracticable owing to the lack of polarimetric guidance in this case (38).

Table 4 summarizes some of the more important derivatives of the four optically active bases under discussion, and indicates their striking similarity in certain respects. The rotatory powers were observed in water for the hydrochlorides and in chloroform for the other derivatives.

Configurationally, *d*-neoisomenthylamine is closely analogous to *d*-neomenthylamine, since it yields partly racemized *d*-Δ³-menthene, and apparently a little *d*-isomenthol, when brought into reaction with nitrous acid. The following relative molecular configurations have accordingly been assigned to the isomenthyl-amines (52):

<pre>
   Me——H   Me——H

   NH₂——H   H——NH₂

   Prβ——H   Prβ——H
</pre>

       d (or *l*)-Iso-   *d* (or *l*)-Neoiso-
        menthylamine   menthylamine
         (XXXIII)   (XXXIV)
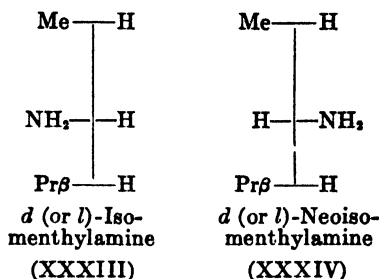
The circumstance that all four bases yield partly racemized *d*-Δ³-menthene, in varying amounts, when treated with nitrous acid, affords a proof of the similar spatial disposition throughout the series of the groups about carbon atom (1), which is the sole asymmetric center in Δ³-menthene. It will be noted that Δ³-menthene appears to be always formed, in lieu of neomenthol or neoisomenthol, in these reactions. In the arguments which have been advanced, "the configurations which have been assigned to these substances are based largely upon the assumption that the stereoisomeride which passes most readily into a particular menthol when treated with nitrous acid is configurationally similar to that menthol. . . . . Thus, *l*-menthylamine and *d*-isomenthylamine yield the largest proportions of *l*-menthol and *d*-isomenthol, respectively, when treated with this reagent. Accepting these processes as the normal ones, the simultaneous formation of partly racemized *d*-Δ³-menthene takes place through a Walden inversion, leading to the intermediate production of

d-neomenthol and an optically active neoisomenthol, respectively; these alcohols, since they possess a hydrogen atom (4) in the *cis*-configurative position to the hydroxyl group (3), then undergo dehydration. The formation of partly racemized d-Δ^3-menthene as the main product in the remaining instances of d-neomenthyl-amine and d-neoisomenthylamine is accordingly regarded as the normal procedure" (52). Recent investigations (56) have shown that d-neomenthylamine reacts much more rapidly than l-menthylamine with acetic anhydride, propionic anhydride, benz-aldehyde and anisaldehyde: additional support is thus lent to the relative configurations which have been deduced from the reactions with nitrous acid.

All the menthylamines are liquids with a characteristic basic odor. Their physical constants, which have lately been deter-mined (56), are closely similar. They absorb carbon dioxide readily, forming solid carbonates. Three out of the four hydro-chlorides included in table 4 display almost identical rotatory powers in aqueous solution. In general, the properties of the stereoisomeric menthylamines are so alike as to prevent the separation of mixtures of these bases formed in the reduction of piperitoneoxime, etc. (53).

The optical resolution of externally compensated menthyl-amines presents peculiar difficulties, which appear to be associated with the abnormal molecular rotatory powers exhibited in dilute aqueous solution by the salts of the optically active bases with strong optically active acids (54). Further light upon this interesting problem may be anticipated from a study of N-alkylated menthylamines and quaternary menthylammonium compounds (38).

A comparison of the ten salicylidenementhylamines which are now known has shown that the derivatives of the menthylamines and isomenthylamines are phototropic, while those of the neo- and neoiso-menthylamines are not (52). The reversible color-change is shown most distinctly by salicylidene-l- and -d-menthyl-amine, which are deep orange in bright light and pale yellow in subdued light. No other example of a phototropic distinction between stereoisomers appears to have been observed (57).

From the data summarized in table 4, it is seen that the derivatives of menthone (*trans*) possess greater rotatory powers than those of isomenthone (*cis*). The optical relationships are more
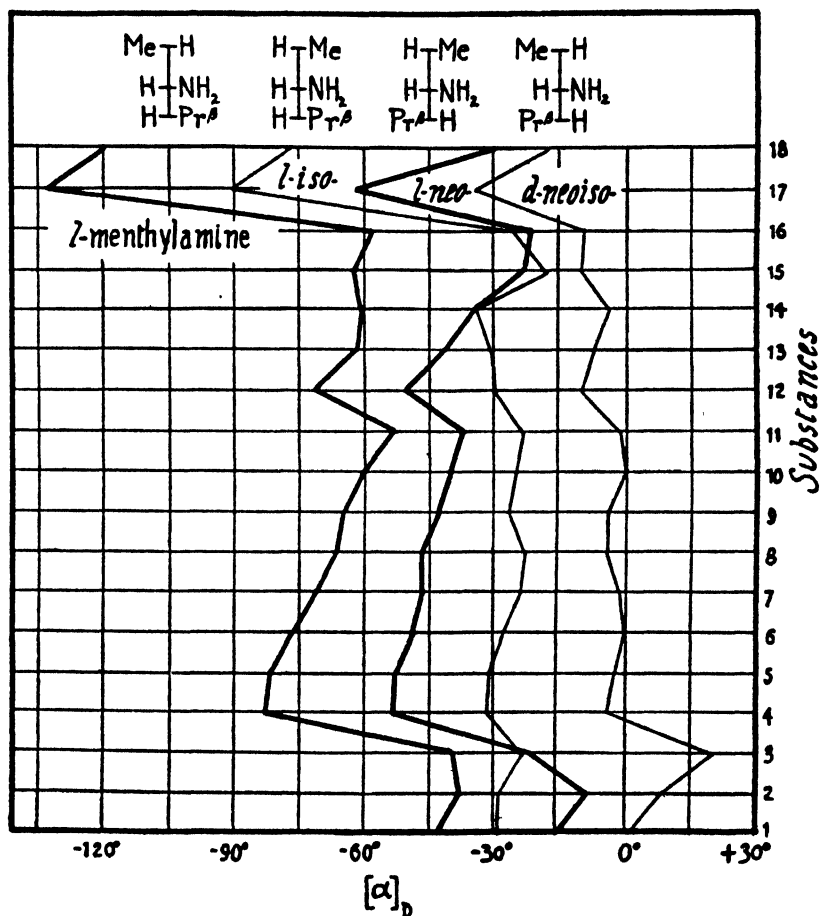
Fig. 11. Graphical Representation of the Specific Rotatory Powers of the Four Series of Stereoisomeric Menthylamines and Certain of Their Derivatives (see Table 5)

fully evident from the graphical representation of figure 11, in which observations of specific rotatory power (56) are summarized for each base, without solvent (No. 1) and dissolved in chloro-

form (No. 2); for the respective hydrochlorides, dissolved in water (No. 3); and for 15 other derivatives of each base (enumerated in table 5), dissolved in chloroform ($c = 1.0$, approximately). In order to simplify the representation, the values of $[\alpha]_D$ observed for d-neo- and d-iso-menthylamine have been changed from positive to negative, so that the values in figure 11 refer to l-, l-neo-, l-iso- and d-neoiso-menthylamine, respectively. The following are among the more important general conclusions to be drawn from the diagram:

(i) A generic relationship is shown by the four curves.

(ii) The two bases derived from menthone (indicated by thicker lines) display a marked family likeness, and so do the two bases derived from isomenthone.

(iii) d-Neoisomenthylamine, in spite of the dextro-rotation shown by the free base and its hydrochloride, belongs to the l-series, and the dextro-rotation in question is in keeping with the general trend of the diagram.

(iv) The bases of the l-series are characterized by the presence of the configurational unit, $H|NH_2$.

(v) Apart from the anomaly created by the intrusion of d-neoisomenthylamine and its hydrochloride into the dextro-rotatory zone, reversal of the asymmetry of carbon atom (3), carrying the characteristic amino group, changes the sign of the optical rotation; on the other hand, reversal of the asymmetry of carbon atom (1) or (4) leaves the sense of the rotation unaltered.

(vi) There is an increasing change in the magnitude of the optical rotation upon passing from l-menthylamine in succession to l-neo-, l-iso- and d-neoiso-menthylamine: that is to say, in this sequence an increasing optical disturbance is created by reversing the asymmetry of carbon atoms (1) and (4) together; carbon atom (1) alone; carbon atom (4) alone; and carbon atom (3) alone.

(vii) The curve of d-neomenthylamine forms a somewhat distorted reflection of the curve of l-menthylamine, and the distortion increases upon passing in succession to d-iso- and l-neoiso-menthylamine.

(viii) The lowest rotatory powers are given by iso- and neoiso-

menthylamine and their derivatives: the corresponding molecular configurations display, respectively, the greatest symmetry of distribution of like (H) and similar (Me and Prβ) groups.

An inspection of the optical rotatory powers of the acetyl derivatives of l-, d-neo-, d-iso- and d-neoiso-menthylamine (table 4) shows that the sum of any two of the values is approximately equal in magnitude and opposite in sign to the sum of the other two.   The additional observations summarized in table 5 indicate

TABLE 5

Values of $[\alpha]_D$ *for menthylamines and derivatives* (*in chloroform, unless otherwise indicated*)

REFERENCE NUMBER AND NAME OF DERIVATIVE	l-	d-Neo-	d-Iso-	d-Neoiso-	$l-$ + d-Neo-	d-Iso- + d-Neoiso-
1. Base (no solvent).......	$-43.2°$	$+15.1°$	$+28.8°$	$+0.28°$	$-28.1°$	$+29.1°$
2. Base...................	-38.3	$+8.7$	$+28.1$	$+8.7$	-29.6	$+36.8$
3. Hydrochloride (water).	-36.6	$+21\ 5$	$+23.6$	$+20.9$	-15.1	$+44.5$
4. Formyl...............	$-83\ 8$	$+53\ 8$	$+31\ 3$	-3.9	-30.0	$+27.4$
5. Acetyl...	$-81\ 7$	$+53\ 0$	$+30.7$	-2.6	-28.7	$+28.1$
6. Propionyl...	-76.6	$+48.3$	$+27.7$	0.0	-28.3	$+27.7$
7. Butyryl	$-70\ 9$	$+46\ 8$	$+23.9$	-1.0	-24.1	$+22.9$
8. Isobutyryl...........	$-66\ 5$	$+47.5$	$+22.8$	-3.7	$-19\ 0$	$+19.1$
9. Valeryl...............	$-64\ 7$	$+42\ 8$	$+27.0$	-4.1	-21.9	$+22.9$
10. Caproyl...............	-60.0	$+40\ 0$	$+24.9$	0.0	-20.0	$+24.9$
11. Capryl...............	$-53\ 2$	$+36.7$	$+23.3$	$-1\ 2$	-16.5	$+22.1$
12. Chloroacetyl..........	$-71\ 9$	$+50\ 7$	$+30\ 0$	-9.8	-21.2	$+20.2$
13. Bromoacetyl.........	$-61\ 6$	$+40\ 9$	$+30.3$	-7.5	-20.7	$+22.8$
14. Phenylacetyl..........	-60.4	$+34\ 5$	$+33.3$	-3.4	-25.9	$+29.9$
15. Benzoyl...............	$-62\ 8$	$+22\ 7$	$+18.3$	-10.4	-40.1	$+7.9$
16. Anisoyl...............	-57.7	$+21.1$	$+25\ 3$	-9.5	-36.6	$+14\ 8$
17. Benzylidene...........	-132.5	$+61\ 7$	$+90\ 7$	$-34\ 2$	$-70\ 8$	$+56.5$
18. Salicylidene..........	$-119\ 2$	$+30.0$	$+77.6$	-17.9	-89.2	$+59.7$

that this curious relationship holds generally for derivatives of the type $R \cdot CH_2 \cdot CO \cdot NH \cdot R'$, and for the free bases; it obtains, moreover, for $[\alpha]_{5461}$, as well as for $[\alpha]_D$.   When R is phenyl and the adjacent methylene group is simultaneously eliminated, the relationship fails; also, it is not evident in derivatives of the type $R \cdot CH:NR'$.   Thus, with derivatives of the type $R \cdot CH_2 \cdot CO \cdot NHR'$, if three of the values of $[\alpha]_D$ are known, the fourth value can be calculated empirically with a close approach to

accuracy. The result suggests the operation of a principle of optical superposition among these stereoisomeric series of derivatives, and this matter may now be discussed.

Selecting a suitable derivative, e.g. the acetyl derivative, and superposing the four configurations in question (XXXI, XXXII, XXXIII and XXXIV), it is seen from table 5 that the algebraic sum of the four values of $[\alpha]_D$ approximates to zero. In the process of superposition, the optical effects of the asymmetric groups (3) and (4) would appear to undergo a mutual neutralization, owing to the opposed spatial dispositions of these groups in the various molecules. The possibility of such an annulment is not immediately obvious, however, for the asymmetric group (1), which has the same spatial disposition (i.e. Me|H) in all four configurations. Unless the approach to a zero value is purely fortuitous, which appears improbable, a simple explanation may be sought in the assumption that the asymmetric group (1) exerts a numerically constant rotational effect in all four configurations, the positive or negative sense of which is determined by the nature of the attached complex group (*vide infra*). If, in two of the four instances, the effect is negative, and in the other two positive, the origin of the zero value is explained.

By taking the mean optical rotation of the *l*- and *d*-iso-acetyl derivatives, the rotational effect of the asymmetric group (1) is evaluated at 25.5 units, and the mean optical rotation of the *l*-neo- and *l*-neoiso-acetyl derivatives gives the almost identical result, 25.2 units; the average value is thus 25.4 units. Similarly, the average value for the combined rotational effect of the remaining asymmetric centres, (3) and (4), is 56.2 units for *cis*-H and 27.8 units for *trans*-H. By adding −25.4 units to −56.2 and +56.2 units, respectively, the values of $[\alpha]_D$ for the *l*- and *d*-iso-acetyl derivatives are regained; correspondingly, the values for the *l*-neo- and *l*-neoiso-acetyl derivatives are regained by adding −25.4 units to −27.8 and +27.8 units, respectively.

Proceeding now to a generalization, it seems that in each of the eight stereoisomeric acetylmenthylamines the asymmetric group (1) has a constant value of 25.4 units of specific rotational power (in chloroform solution, for sodium light). When the configura-

tion Me|H is attached to H|NHAc or to NHAc|H it exerts a
            H|Prβ   Prβ|H
levo-rotatory effect; but when the same configuration is attached
to   H|NHAc or to NHAc|H   its effect, although equal in magni-
   Prβ|H   H|Prβ
tude, is dextro-rotatory. Further, the complex asymmetric groups
H|NHAc and   H|NHAc have respective constant values of
H|Prβ   Prβ|H
—56.2 and —27.8 units of specific rotational power.   From the
three constants, 25.4, 56.2 and 27.8, it is possible to calculate

TABLE 6

Specific rotational values ([α]$_D$ in chloroform, unless otherwise indicated) for asymmetric groups in the menthylamines and some of their derivatives

REFERENCE NUMBER AND NAME OF DERIVATIVE	Me|H	H|NHR H|Prβ	H|NHR Prβ|H	H|NHR	H|Prβ
1. Base (no solvent)	±7 5	−36 0	−7 4	−21.7	−14.3
4. Formyl	25 6	−57 6	−28 9	−43 3	−14.4
5. Acetyl	25 4	−56 2	−27 8	−42 0	−14.2
6. Propionyl	24 3	−52.2	−24 2	−38 2	−14.0
7. Butyryl..	23 2	−47 4	−23 9	−35 7	−11.8
8. Isobutyryl........	21 9	−44 7	−25 6	−35.2	−9.6
9. Valeryl	19 1	−45 9	−23 5	−34 7	−11.2
10. Caproyl	18 8	−42 5	−20.0	−31.3	−11.3
11. Capryl	16 4	−38 3	−19 0	−28 7	−9.7
12. Chloroacetyl	20 7	−51 0	−30 3	−40.7	−10.4
13. Bromoacetyl	16 2	−46 0	−24 2	−35 1	−10.9
14. Phenylacetyl	14 6	−46 9	−19 0	−33 0	−14.0

the value of [α]$_D$ for any acetylmenthylamine whose relative
molecular configuration is known.   A similar statement applies
to any menthylamine derivative of the type R·CH$_2$·CO·NHR'
which has been examined up to the present (see table 6).   As an
illustrative example, the configuration of acetyl-*d*-menthylamine
may be selected: H|Me   The complex configurational unit
                    NHAc|H .
                    Prβ|H
NHAc|H has the value +56.2; Me|H attached to it has the value
   Prβ H
—25.4, so that obviously the value for H|Me is +25.4.   Thus,
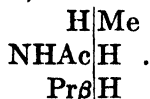
only. Briefly, in each of these two cases the molecule behaves as a system of two asymmetric centers; that is, groups (3) and (4) act as a composite center when their mutual configurational relationship undergoes no change.

But when one only of the groups (3) and (4) is turned through 180°, two adjustments have to be made, because the asymmetry of the turned group is reversed with respect to both of the other asymmetric groups. Thus, the rotational value of group (1), as well as that of the turned group, has to be reversed, since the molecule behaves in this instance as a system of three distinct asymmetric groups.

These conclusions are closely bound up with the circumstance that there is no alteration in the immediate environment of group (1), or in that of the composite group (3) and (4), when either of these two configurational units is turned through 180°.

TABLE 10

Physical characteristics of the known menthols

	MENTHOLS			NEOMENTHOLS			ISOMENTHOLS		
	d-	*l-*	*dl-*	*d-*	*l-*	*dl-*	*d-*	*l-*	*dl-*
m. p.........	43°	43°	34°	oil	oil	51°	81 5°	80 5°	53.5°
$[\alpha]_D$.........	+49°	−49°		+19 6°	−19 6°		+27 0°	−24 1°	
	(in alcohol)			(no solvent)			(in alcohol)		

The sense of the optical rotational influence exerted by each of the three asymmetric groups in the molecular configurations of the substances which have been discussed may be summarized as in table 9.

The menthols

As already indicated, the three stereoisomeric forms of ordinary menthol were first made available through the work of Pickard and Littlebury (10), and it has been shown in the preceding section that *d-, l-* and *dl-*isomenthol may be prepared from *l-, d-* and *dl-*piperitone, respectively, through the corresponding isomenthylamines (table 3). The physical characteristics of the known menthols are summarized in table 10.

From their apparent relationship to the menthylamines, out-

lined above, the menthols have been provisionally assigned the following relative molecular configurations (58):

```
  Me ——H        Me ——H        Me——H         Me——H
    |             |             |             |
    |             |             |             |
H—|²-OH      HO—|—H        HO—|—H         H—|—OH
    |             |             |             |
H——|⁴-Prβ     H——|—Prβ     Prβ—|—H       Prβ——|—H
  l (or d)-     d (or l)-Neo-  d (or l)-Iso-  d (or l)-Neo-
  Menthol       menthol        menthol        isomenthols
  (XXXV)        (XXXVI)        (XXXVII)       (XXXVIII)
```
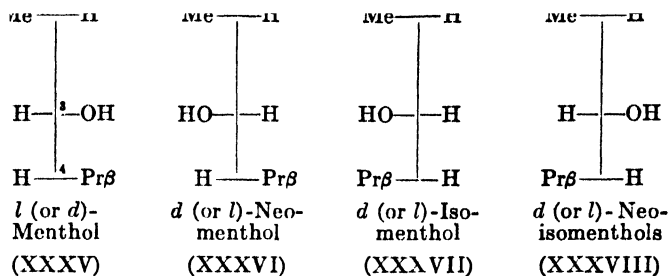
Vavon and Couderc (59) consider —OH(3) to be in the *trans*-position to —H(4) in neomenthol, since this alcohol esterifies more slowly than menthol. Zeitschel and Schmidt (6), however, found that neomenthol is dehydrated much more readily than menthol, forming Δ^3-menthene. The balance of the evidence thus appears to favor the configurations given above. The externally compensated forms of menthols and isomenthols have lower melting points than their active components, but in the neo-series this relationship is reversed; possibly, therefore, *dl*-neoisomenthol will prove to possess a higher melting point than its active components. The melting-point curve of mixtures of *d*- and *l*-isomenthol is typical of a conglomerate (46). Various unsubstantiated references to racemic menthols and menthones have been made by Bedos (60), Fleury and Seel (61) and others, but up to the present the neoisomenthols appear not to have been prepared.

The main approach yet discovered from optically active piperitone to optically active menthol is by the route: *l* (or *d*)-piperitone → *l* (or *d*)-menthone → *l* (or *d*)-menthoneoxime → *l* (or *d*)-menthylamine → *l* (or *d*)-menthol (table 3); alternatively, the menthone may be reduced with sodium and alcohol. The practical value of these processes is seriously impaired by the circumstance that *l* (or *d*)-menthone prepared in this way is associated with *d* (or *l*)-isomenthone. *dl*-Menthol, however, may be prepared from piperitone by direct reduction (*vide infra*); and

since *dl*-menthol is also available from other primary sources, such as *m*-cresol and thymol, the most satisfactory method at present apparent for the production of *d*-menthol departs from *dl*-menthol and proceeds by way of *dl*-menthone, *dl*-menthone-oxime, *dl*-menthylamine and *d*-menthylamine (*vide supra*). The preparation of *d*-menthol in quantity by the direct optical resolution of *dl*-menthyl hydrogen phthalates (10) is impracticable.[2]

Piperitone may be reduced electrolytically to isomenthone (62), and no doubt the reduction might be intensified to yield menthols. When active or externally compensated piperitone is reduced with

TABLE 11

The conversion of dl-piperitone into dl-menthone

dl-PIPERITONE

(sodium + alcohol)   (catalytic hydrogenation)

dl-Isomenthols + *dl*-Menthols $\xrightarrow{\text{(chromic acid)}}$ *dl*-Isomenthone + *dl*-Menthone

(sodium + alcohol)

dl-Isomenthols + *dl*-Menthols

(separate)

dl-Menthol

(chromic acid)

dl-Menthone (pure)
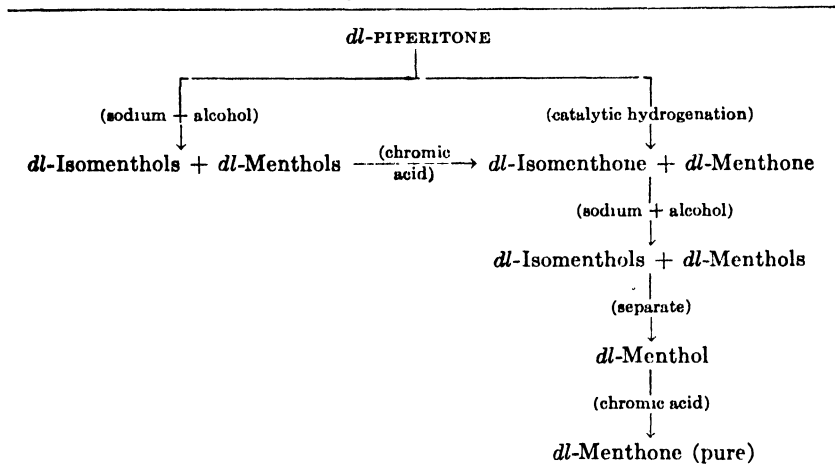
sodium and alcohol it yields a mixture of inactive menthols consisting chiefly of isomenthols (47), but containing a little *dl*-menthol (46). The yield of *dl*-menthol may be improved by oxidizing the product and reducing the equilibrated mixture of *dl*-menthone and *dl*-isomenthone; alternatively, the last-named mixture may be prepared by the catalytic hydrogenation and electrolytic reduction of *dl*-piperitone. By separating and oxidizing the crystalline *dl*-menthol, it is thus possible to pass from *dl*-

[2] A novel method for the preparation of *d*-menthol from *dl*-menthol, in useful quantities, has recently been devised in the S. Andrews laboratories (38).

piperitone to pure *dl*-menthone.   The main operations are summarized in table 11.

Menthenes, menthadienes and menthenols

Since *d*-Δ³-menthene is formed by the action of nitrous acid on *l*-, *d*-neo-, *d*-iso- or *d*-neoiso-menthylamine, the enantiomers of these bases would yield *l*-Δ³-menthene.   In all these instances the hydrocarbon is partly racemized, e.g. the product from *d*-neomenthylamine (52), having $[\alpha]_D$ + 58.6° (in ether), contains almost 80 per cent of *d*-Δ³-menthene, assuming that the value +106.6° of a specimen prepared by Tschugaev's xanthic ester method (32) is characteristic of the optically pure substance. Partly racemized Δ³-menthenes are produced also by the action of thionyl chloride, phosphorus chlorides and other dehydrating agents upon menthols (6) (63); thus, *l*-menthol when treated with phosphorus trichloride yielded *d*-Δ³-menthene with $[\alpha]_D$ +22.3° (64).   Wallach prepared a specimen having $[\alpha]_D$ +89.3° by distilling *l*-menthyltrimethylammonium hydroxide (51); more recently, Patterson and McAlpine (65) have shown that feebly dextro-rotatory Δ³-menthene is produced by distilling *l*-menthylbenzene sulfonate under diminished pressure:

CHMe   CHMe

H₂C   CH₂   H₂C   CH₂
  | | | | + Ph · SO₃H
H₂C   CH · O · SO₂Ph   H₂C   CH

CH · CHMe₂   C · CHMe₂

l-Menthylbenzene   Δ³-Menthene
sulfonate
(XXXIX)   (XL)
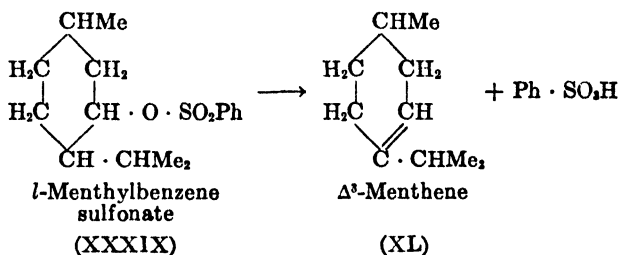
The action upon *l*-menthone of magnesium methyl iodide has been examined by Wanin (66) and also by Zelinsky (67); and Murat (68) applied magnesium phenyl bromide to the same ketone.   Recent work in this field (43) has shown that both *l*-menthone and *d*-isomenthone react with magnesium methyl, ethyl and phenyl halides to form 3-substituted menthan-3-ols; these tertiary alcohols, when heated with anhydrous oxalic acid, undergo dehydration to produce 3-substituted Δ³- menthenes:

$$
\begin{array}{ccc}
\text{CHMe} & \text{CHMe} & \text{CHMe} \\
\text{H}_2\text{C} \quad \text{CH}_2 & \text{H}_2\text{C} \quad \text{CH}_2 & \text{H}_2\text{C} \quad \text{CH}_2 \\
\text{H}_2\text{C} \quad \text{CO} & \longrightarrow \quad \text{H}_2\text{C} \quad \text{C(OH)}\cdot\text{R} & \longrightarrow \quad \text{H}_2\text{C} \quad \text{CR} \\
\text{CH}\cdot\text{CHMe}_2 & \text{CH}\cdot\text{CHMe}_2 & \text{C}\cdot\text{CHMe}_2
\end{array}
$$

Menthones	3-Homologues of menthanol-3	3-Homologues of Δ^3-menthene
(XLI)	(XLII)	(XLIII)
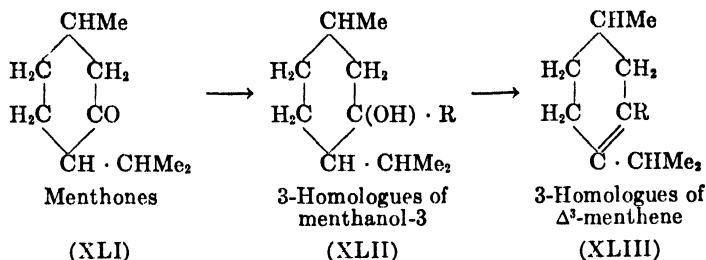
From the data summarized in table 12, it is seen that the two ketones give rise to distinct products; these, however, cannot be regarded as stereochemically homogeneous. The alcohol in each case is probably a mixture of four of the eight possible optically active modifications of constitution (XLII), and the hydrocarbons (especially those from d-isomenthone) appear to be partly racemized homologous menthenes (XLIII).

Piperitone, in reaction with Grignard reagents, was found to yield 3-alkyl-1,3-terpinenes directly, the intervening menthenols not being isolable. This result points' to the interesting conclusion that a ready elimination of water occurs from these homologues of piperitol (XLV), owing to the activation of the tertiary hydroxyl group by the adjacent ethylene linking:

$$
\begin{array}{ccc}
\text{CMe} & \text{CMe} & \text{CMe} \\
\text{H}_2\text{C} \quad \text{CH} & \text{H}_2\text{C} \quad \text{CH} & \text{H}_2\text{C} \quad \text{CH} \\
\text{H}_2\text{C} \quad \text{CO} & \longrightarrow \quad \text{H}_2\text{C} \quad \text{C(OH)}\cdot\text{R} & \longrightarrow \quad \text{H}_2\text{C} \quad \text{CR} \\
\text{CH}\cdot\text{CHMe}_2 & \text{CH}\cdot\text{CHMe}_2 & \text{C}\cdot\text{CHMe}_2
\end{array}
$$

Piperitone	Hypothetical inter-mediate menthenols	3-Homologues of 1,3-terpinene
(XLIV)	(XLV)	(XLVI)
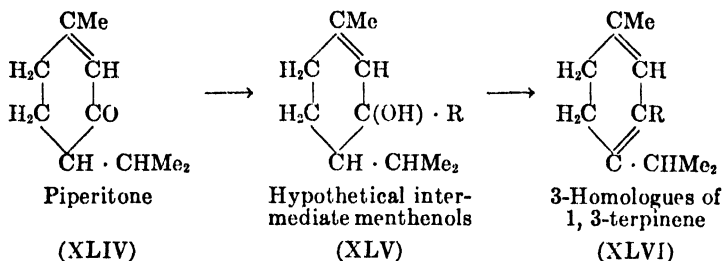
In no case was any action observed to occur between magnesium isopropyl iodide and piperitone or menthones, possibly owing to steric hindrance.

Hydrogenation of the above unsaturated hydrocarbons would lead to 3-substituted menthanes. In addition, evidence is forthcoming (38) which indicates that isomeric series of substituted menthanols, menthenes and menthadienes may be rendered acces-

sible by applying Grignard reagents to tetrahydrocarvone, dihy-
drocarvone, carvotanacetone, pulegone, etc. Moreover, from
carvone it may prove possible to pass to 2-substituted homologues
of *p*-cymene, by isomerizing unsaturated hydrocarbons formed
by Grignardizing the ketone.

BIOGENETIC RELATIONSHIPS

Close structural relationships are often observed to exist
between the individual components of a particular essential oil;
moreover, striking parallels may be discerned in many instances
between groups of substances occurring in two or more oils from

TABLE 12

Menthanols and menthenes derived from l-menthone and d-isomenthone

KETONE	SUBSTITUENT	$[\alpha]_D$ OF SUBSTITUTED MENTHANOL (1-DCM. TUBE)	$[\alpha]_D$ OF SUBSTITUTED MENTHENE
l-Menthone, $[\alpha]_D$ −25.7°	Me	−6 5°	+62.8°
	Et	+1 5	+39.2
	n-Pr	−0.7	+35.9
	Ph	−22.9	+43.5
d-Isomenthone (from *l*-piperitone) $[\alpha]_D$ +69 9°	Me	+27 0	+17.9
	Et	+22 0	+6.8
	Ph	+0 4	+16.3

related species. The consideration of analogies of these two
general types leads invariably to the idea of a common mechanism
of formation, i.e. to the derivation in the plant of related sub-
stances from common chemical ancestors. Thus, Kremers (69),
in 1922, suggested the tentative scheme shown in table 13 to
account for the biogenesis[3] of the two distinctive but closely
related groups of substances found in the oils of American black
mint (*Mentha piperita vulgaris*) and spearmint (*Mentha spicata*).
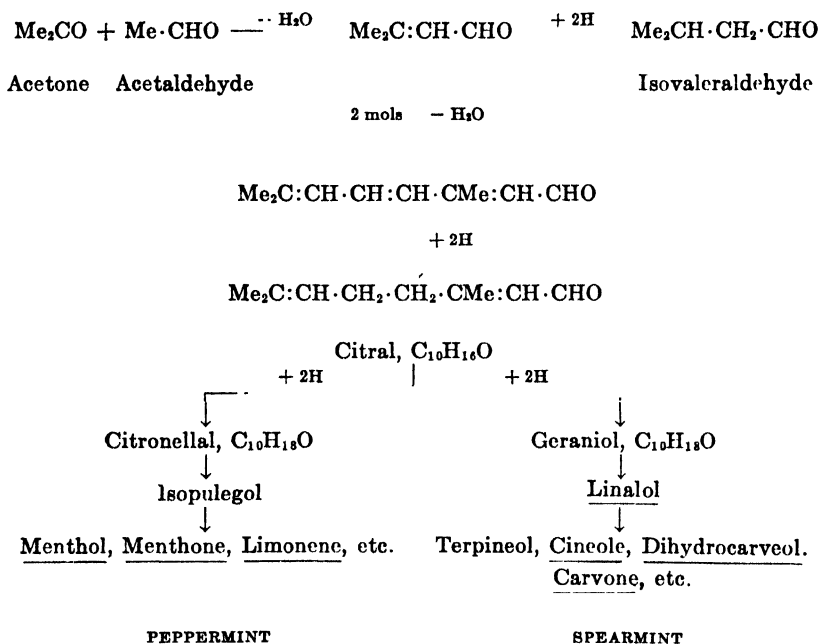
The immediate common ancestor of the two series of substances
shown in this scheme is citral. According to Kremers, the bio-
chemical conditions which in spearmint bring about the reduction
of the aldehyde group are modified in peppermint so as to cause
the reduction of an ethylene linkage. Thus (i) the carvone group

---

[3] That is, the chemical origin *in vivo*, or biological synthesis.

of substances is formed in spearmint and (ii) the menthone group in peppermint. The differential reduction of citral may be accomplished in the laboratory by using (i) sodium amalgam and acetic acid, and (ii) hydrogen in the presence of colloidal palladium; but it is interesting to reflect that in the cross-breeding of closely related species of plants such biochemical divergencies may possibly be due to the operation of Mendelian factors.

TABLE 13

The biogenesis of the two groups of substances found in the oils of American black mint and spearmint

$$Me_2CO + Me \cdot CHO \xrightarrow{-H_2O} Me_2C:CH \cdot CHO \xrightarrow{+2H} Me_2CH \cdot CH_2 \cdot CHO$$

Acetone   Acetaldehyde   Isovaleraldehyde

2 mols $- H_2O$

$$Me_2C:CH \cdot CH:CH \cdot CMe:CH \cdot CHO$$

$+2H$

$$Me_2C:CH \cdot CH_2 \cdot CH_2 \cdot CMe:CH \cdot CHO$$

Citral, $C_{10}H_{16}O$

$+2H$ | $+2H$

Citronellal, $C_{10}H_{18}O$ Geraniol, $C_{10}H_{18}O$

Isopulegol   Linalol

Menthol, Menthone, Limonene, etc.   Terpineol, Cineole, Dihydrocarveol.
                                                               Carvone, etc.

PEPPERMINT   SPEARMINT

The names of substances actually found in the oils are underlined, as are also the two reducible groups in the citral molecule.

From the fact that most of the components of essential oils contain molecular systems of five, ten or fifteen carbon atoms, Astengo (70) regards isovaleraldehyde as their common ancestor and suggests a sequence of the following kind: isovaleraldehyde → isocitronellal → rhodinal, citronellal, geraniol → rhodinol, citronellol, linalol, menthone, isopulegol, citral.

Some of the most arresting biogenetic relationships in the menthone series centre around piperitone. An inspection of the appended formulas shows at once that structurally *l*-piperitone is closely related to *l*-piperitol and *l*-α-phellandrene, with which substances it is associated in the oils of *E. dives*, *E. radiata* and other *Eucalyptus* species:

$$
\begin{array}{cccc}
\text{CMe} & \text{CMe} & \text{CMe} & \text{CMe} \\
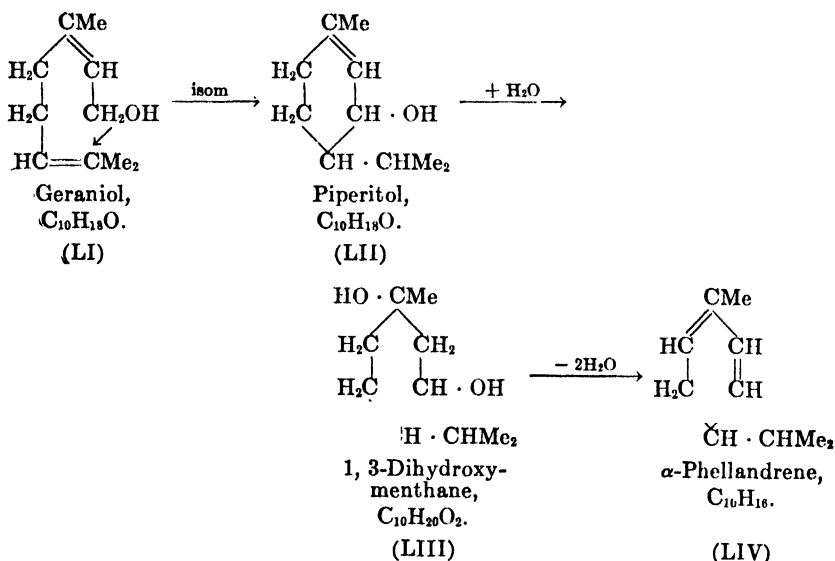\text{H}_2\text{C}\quad\text{CH} & \text{H}_2\text{C}\quad\text{CH} & \text{HC}\quad\text{CH} & \text{H}_2\text{C}\quad\text{CH} \\
\text{H}_2\text{C}\quad\text{CO} & \text{H}_2\text{C}\quad\text{CH}\cdot\text{OH} & \text{H}_2\text{C}\quad\text{CH} & \text{H}_2\text{C}\quad\text{CH} \\
\text{CH}\cdot\text{CHMe}_2 & \text{CH}\cdot\text{CHMe}_2 & \text{CH}\cdot\text{CHMe}_2 & \text{HC}\!-\!\text{CMe}_2 \\
\end{array}
$$

Piperitone	Piperitol	α-Phellandrene	Δ⁴-Carene
(XLVII)	(XLVIII)	(XLIX)	(L)
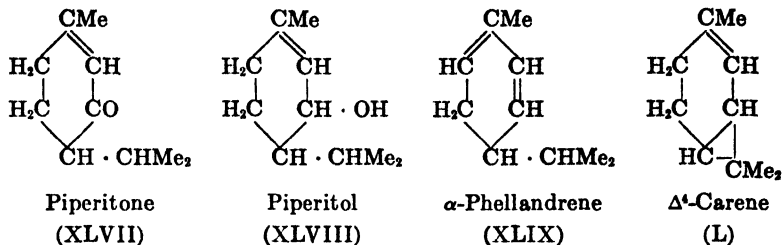
The relationship of *d*-piperitone to *d*-Δ⁴-carene (L), which it accompanies in the oil of *Andropogon Jwarancusa* (22), is not so apparent; but it is extremely significant that the occurrence of *d*-piperitol with *d*-Δ⁴-carene has also been established by Simonsen (71) in the oil of a new species of *Andropogon* growing in the United Provinces. In endeavoring to trace a genetic relationship between Δ⁴-carene and piperitol, Simonsen (71) has pointed out that of the four possible active stereoisomeric forms of piperitol two might be expected to yield α-terpinene upon dehydration, while the other two should give rise to Δ⁴-carene; hence piperitol might conceivably function as the immediate precursor of Δ⁴-carene in these Indian oils. Laboratory experiments showed that *d*-piperitol when dehydrated with magnesium methyl iodide actually yielded α-terpinene, thus behaving similarly to its synthetic homologues (XLV) mentioned in the foregoing section.

It appears to the writer (72) that the clue to the biogenetic relationships of the substances under discussion is to be found in the circumstance that piperitone appears to be invariably associated in *Eucalyptus* oils with a small proportion of geranyl acetate, and it is hoped in due course to submit the ideas derived from this circumstance to experimental investigation, as far as artificial conditions may permit. According to Baker and Smith (13),
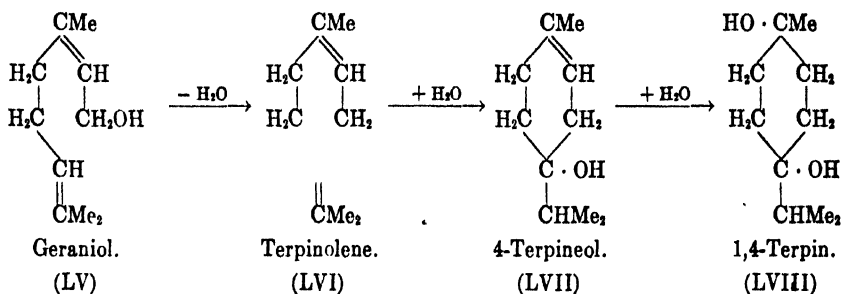
geranyl acetate "passed into *Eucalyptus* through *Angophora*, and as it occurs also in the oils of many of the 'Peppermints' it probably runs through the whole genus *Eucalyptus*, although in some of the oils the amount is very small" (p. 366). An exceptional species, *E. Macarthuri*, yields an oil containing as much as 77 per cent of geranyl acetate, together with a small proportion of free geraniol. Thus, in *E. Macarthuri* the particular chain of biochemical processes is arrested at the formation of geraniol; while in other species the geraniol, under the different conditions prevailing in the plant, may be presumed to undergo further transformations and to function as the precursor of piperitol, piperitone, α-phellandrene and other substances. In the case of *E. dives* the following mechanism may be postulated:

$$
\begin{array}{ccc}
\underset{\substack{H_2C \;\;\; CH \\ | \;\;\;\;\;\; | \\ H_2C \;\;\; CH_2OH \\ \diagdown \;\;\;\;\; \swarrow \\ HC\!=\!CMe_2}}{CMe} & \xrightarrow{\text{isom}} &
\underset{\substack{H_2C \;\;\; CH \\ | \;\;\;\;\;\; | \\ H_2C \;\;\; CH\cdot OH \\ \diagdown \;\;\;\; \diagup \\ CH\cdot CHMe_2}}{CMe} & \xrightarrow{+\,H_2O}
\end{array}
$$

Geraniol, $C_{10}H_{18}O$.   Piperitol, $C_{10}H_{18}O$.

(LI)   (LII)

$$
\underset{\substack{H_2C \;\;\; CH_2 \\ | \;\;\;\;\;\; | \\ H_2C \;\;\; CH\cdot OH \\ \diagdown \;\;\;\; \diagup \\ CH\cdot CHMe_2}}{HO\cdot CMe} \xrightarrow{-\,2H_2O}
\underset{\substack{HC \;\;\; CH \\ || \;\;\;\;\;\; || \\ H_2C \;\;\; CH \\ \diagdown \;\;\;\; \diagup \\ CH\cdot CHMe_2}}{CMe}
$$

1, 3-Dihydroxy-   α-Phellandrene,
menthane, $C_{10}H_{16}$.
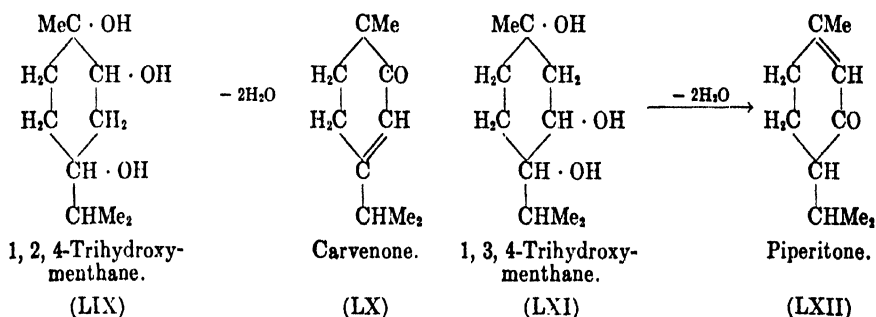$C_{10}H_{20}O_2$.

(LIII)   (LIV)

According to this scheme, the initial product of the isomerization of geraniol, i.e. piperitol, yields (i) α-phellandrene by successive hydration and dehydration, and (ii) piperitone by oxidation. It may be noted that d-α-phellandrene occurs with geraniol in gingergrass oil.

The formation from geraniol of 4-terpineol, which has recently been found in certain specimens of the oil of *E. dives*, and its
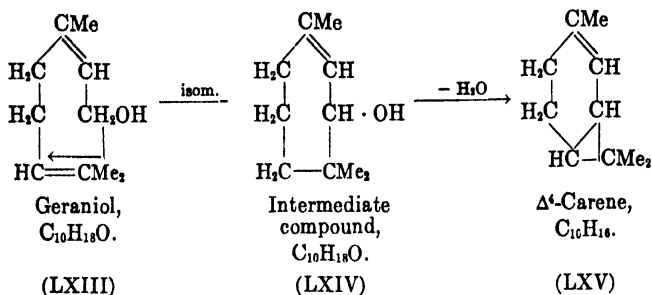
subsequent hydration to 1,4-terpin, may also be readily explained in terms of the above scheme; in this instance terpinolene is possibly, although not necessarily, an intermediate product in the series of changes:

<pre>
     CMe   CMe   CMe   HO·CMe
    /   \   /   \   /   \   /   \
 H₂C   CH   - H₂O   H₂C   CH   + H₂O   H₂C   CH   + H₂O   H₂C   CH₂
  | | -----> | | -----> | | -----> | |
 H₂C   CH₂OH   H₂C   CH₂   H₂C   CH₂   H₂C   CH₂
    \   /   \   /   \   /   \   /
     CH   ‖   C·OH   C·OH
     ‖   CMe₂ | |
     CMe₂   CHMe₂   CHMe₂
  Geraniol.   Terpinolene.   4-Terpineol.   1,4-Terpin.
    (LV)   (LVI)   (LVII)   (LVIII)
</pre>

No members of the carvone series have been discovered in *Eucalyptus* oils. It is therefore of particular interest that a passage from *Eucalyptus* components to this series is provided by the observation (73) that 1,2,4-trihydroxymenthane (m.p. 113–5°), obtained from 4-terpineol by the action of cold permanganate, may be dehydrated to carvenone by a reaction which is reminiscent of Wallach's synthesis of piperitone (34) from 1,3,4-trihydroxymenthane (m.p. 120°):
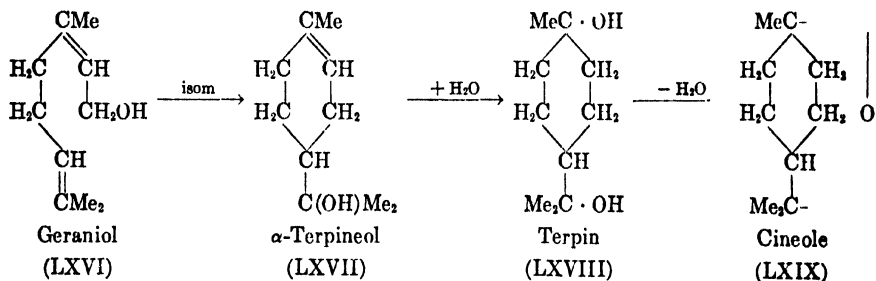
<pre>
    MeC·OH   CMe   MeC·OH   CMe
    /   \   /   \   /   \   /   \
 H₂C   CH·OH   H₂C   CO   H₂C   CH₂   - 2H₂O   H₂C   CH
  | | - 2H₂O | | | | -----> | |
 H₂C   CH₂   H₂C   CH   H₂C   CH·OH   H₂C   CO
    \   /   \   /   \   /   \   /
     CH·OH   C   CH·OH   CH
     | ‖ | |
     CHMe₂   CHMe₂   CHMe₂   CHMe₂
 1,2,4-Trihydroxy-   Carvenone.   1,3,4-Trihydroxy-   Piperitone.
    menthane.   menthane.
     (LIX)   (LX)   (LXI)   (LXII)
</pre>

Possibly the most interesting biogenetic association of piperitone and piperitol is with Δ⁴-carene, and here geraniol may be regarded as the immediate precursor not only of the alcohol and ketone, as already shown, but also of the bridged hydrocarbon:
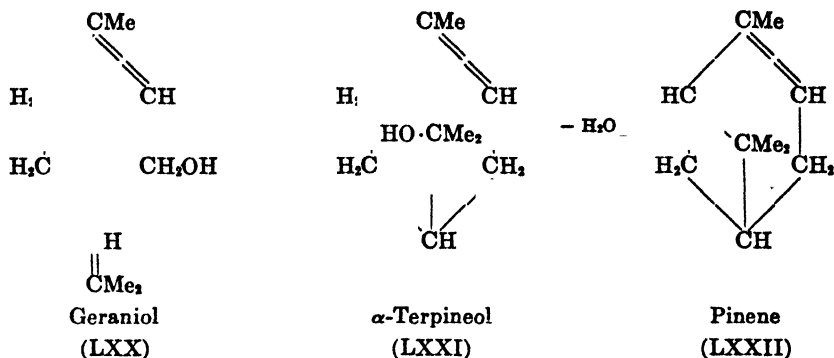
CMe   CMe   CMe
H₂C   CH   isom.   H₂C   CH   − H₂O   H₂C   CH
H₂C   CH₂OH   ──────   H₂C   CH·OH   ──────→ H₂C   CH
HC═CMe₂   H₂C─CMe₂   HC─CMe₂

Geraniol,   Intermediate   Δ⁴-Carene,
C₁₀H₁₈O.   compound,   C₁₀H₁₆.
                       C₁₀H₁₈O.

(LXIII)   (LXIV)   (LXV)

The simple mechanism indicated in the above representation demands only the transference of a hydrogen atom to form an unstable 7-carbon ring-compound, which would then be readily dehydrated to Δ⁴-carene. In the light of this idea, it should be of interest to search systematically for Δ⁴-carene in geraniol oils.

The mechanisms which have been outlined could obviously be extended to the production of menthone and menthol from geraniol, and although these substances have not been found in *Eucalyptus* oils they are associated with piperitone in Japanese peppermint oil (23). It seems possible also that cineole, another of the main components of *Eucalyptus* oils, may be derived from geraniol, by way of α-terpineol and terpin:

CMe   CMe   MeC·OH   MeC─
H₂C   CH   H₂C   CH   H₂C   CH₂   H₂C   CH₂
H₂C CH₂OH   H₂C   CH₂   H₂C   CH₂   H₂C   CH₂   O
 CH   CH   CH   CH
 ‖ | | |
 CMe₂   C(OH)Me₂   Me₂C·OH   Me₂C─
Geraniol   α-Terpineol   Terpin   Cineole
(LXVI)   (LXVII)   (LXVIII)   (LXIX)

(isom →, + H₂O →, − H₂O →)

The remaining constituent of *Eucalyptus* oils of the first importance is pinene (table 1). Whether this *meta*-bridged hydrocarbon may be correlated biogenetically with geraniol is problematical. It may be pointed out, however, that the 6-methylene group of α-terpineol may be regarded as activated by the αβ-ethylenic linkage, as in piperitone and Δ⁴-menthenone (*vide supra*); further, according to Thorpe and Ingold's modification of Baeyer's

strain theory, the grouping >CMe₂ confers stability upon a 4-carbon ring-system, and hence presumably facilitates its formation. Thus, although it has not proved possible to proceed from α-terpineol to pinene *in vitro*, it may well be that *in vivo* some such scheme as the following may take place:

CMe   CMe   CMe
  \\   \\   / \\
H₂   CH   H₂   CH   HC   CH
                              HO·CMe₂   − H₂O   \`CMe₂ |
H₂C   CH₂OH   H₂C   CH₂   H₂C | CH₂
                                      \|/   \   /
   H   CH   CH
   ‖
  CMe₂
  Geraniol   α-Terpineol   Pinene
  (LXX)   (LXXI)   (LXXII)

To sum up, it is evident that geraniol (or, possibly, its geometrical isomer, nerol) possesses strong claims to be regarded as the immediate precursor of piperitol, piperitone, Δ⁴-carene and other substances which occur in this association in essential oils. All these substances may be readily depicted as transformation products obtained by applying simple processes of isomerization, hydration, dehydration, oxidation and reduction to the parent compound. The latter, in turn, may originate, in accordance with the conceptions of Kremers, Astengo and others, from such simple units as isovaleraldehyde: from this point of view it is interesting that isoamyl alcohol, valeraldehyde and esters of valeric acid have all been found in *Eucalyptus* oils (13).

In conclusion, the implied aptitude of geraniol to function in nature as a precursor of so many other substances may be attributed largely to the unusual conformation of its molecule, which possesses a structure (A), ·CMe:CH·CH₂OH, consisting of a primary alcohol group activated by an αβ-ethylenic linkage and situated in spatial proximity to a 'second active grouping (B), ·CH:CMe₂, containing another double bond. Migration of a hydrogen atom, in the 'nascent' molecule of geraniol, from the primary alcohol group of (A) to one side of the double bond of

(B) leads to piperitol, piperitone and α-phellandrene; migration of the same hydrogen atom to the other side of the double bond leads to Δ⁴-carene. Thus, while the migration in *Eucalyptus* species is limited to one direction, in *Andropogon* species it occurs simultaneously in both directions. Even in the migration common to both families, an exceedingly refined distinction is still apparent, since from the symmetric molecule of geraniol the Australian trees produce the left-handed variety of piperitol and of piperitone, while the Indian grasses give rise to the right-handed forms of these asymmetrically constituted substances. The excessively delicate control of molecular transformation which is here implied appears to be a prerogative of the living organism. The organic chemist is powerless to effect such subtle differentiations by artificial means. At the present stage of our knowledge, the finer manifestations of organic synthesis appear to be inseparably associated with the life-processes.

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THE CHEMISTRY OF RUBBER

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CONTENTS

I. LATEX AND CRUDE RUBBER

1. Introduction

Everyone is familiar with the pictures of the *seringueiro* with his slender hatchet, in the heart of the Amazon jungle,

cutting into the bark of the giant *Hevea*[1] *brasiliensis*, and of the typical coolie, carefully tapping descendants of the Amazon *Hevea* trees on the well-kept plantations in the Far East, both obtaining the milky fluid or latex that yields the crude rubber of commerce. Everyone is also familiar with the rise of Brazil as the dominating

TABLE 1

Production of crude rubber in long tons (1a)

YEAR	PLANTA- TION	AMAZON VALLEY	OTHER	TOTAL	U S NET IMPORTS	RATIO IMPORTS/ TOTAL	TONS OF RUB- BER EXPORTED AS LATEX (CALCULATED ON BASIS OF 3 LBS TO THE GALLON) NOT INCLUDED IN THE TOTAL
1904	4	26,750	27,136	53,890			
1910	10,916	37,938	45,096	93,950	42,254	0 45	
1911	17,501	35,970	40,584	94,055	41,901	0 44	
1912	33,306	41,619	39,351	114,276	55,979	0 49	
1913	53,644	35,659	30,820	120,123	52,025	0 43	
1914	74,567	33,001	15,585	123,173	62,266	0 51	
1915	116,370	34,610	19,846	170,826	99,011	0 58	
1916	161,842	30,997	21,250	214,089	117,611	0 55	
1917	221,452	33,461	23,227	278,140	179,255	0 64	
1918	181,061	22,303	16,320	219,684	143,386	0 65	
1919	348,990	32,726	18,015	399,731	238,407	0 60	
1920	305,106	23,216	13,672	341,994	249,520	0 73	
1921	277,516	17,164	6,938	301,618	179,736	0 60	
1922	379,520	19,542	7,336	406,398	296,394	0 73	
1923	380,271	16,765	11,683	408,719	301,527	0 74	2,124
1924	393,931	23,165	9,082	426,178	319,103	0 75	1,902
1925	478,428	25,298	13,797	517,523	385,596	0 75	5,028
1926	581,215	24,298	16,017	621,530	399,972	0 64	2,850
1927	562,059	28,782	15,633	606,474	403,493	0 67	2,160
1928	621,782	21,129	10,690	653,601	407,564	0 62	4,167
1929*	813,000	21,000	9,000	843,000	475,000	0 56	

* Estimated figures.

factor in the production of the world's supply of crude rubber, and with the wonderful growth of the plantation industry, until in 1913 it finally outstripped Brazil and gave to the world an ever increasing supply of rubber without which the great automotive industry could not have continued its remarkable development.

[1] Pronounced Hēv-ea.

One is probably not so familiar with the fact that, whereas the plantations produced for the market only four tons of rubber in 1900, Brazil and the rest of the tropical world produced 54,000 tons; that in 1910 when the plantations produced 11,000 tons, Brazil was at its peak with 38,000 tons and the rest with 45,000 tons; and that in 1929, the plantations produced the enormous quantity of 813,000 tons, while Brazil and the rest produced only 30,000 tons altogether. Two-thirds of the total production

TABLE 2

Estimated acreage of the estate and native rubber plantations (2)

	1922 ACRES	1927 ACRES	1928 ACRES
British Colonies:			
Malaya	2,268,000	2,632,000	2,714,000
Ceylon	443,000	499,000	534,000
India and Burma	126,000	147,000	167,000
North Borneo	59,000	93,000	288,000
Sarawak, etc.	81,000	113,000	
Total	2,977,000	3,484,000	3,703,000
Other Middle East:			
Dutch Estates	940,000	1,199,000	2,899,000
Dutch Natives	500,000	1,300,000	
Indo-China	83,000	137,000	250,000
Siam	30,000	43,000	150,000
Total	1,553,000	2,679,000	3,299,000
Rest of the World (Liberia, etc.)			65,000
Grand Total	4,530,000	6,163,000	7,067,000

is annually imported into the United States, and half of this finds its way to Akron, Ohio,—the great manufacturing center of the rubber world. Over three-quarters of the total production is made up into automobile tires and tubes.

The price of crude rubber has fluctuated much. It was around $3.00 a pound in the great rise of 1910 and dropped to 14 cents a pound during the slump of 1921–22. Now, it sells for 15–20 cents a pound. The great rubber industry of the United States manufactures annually goods valued at over a billion dollars ($1,225,077,114 in 1927).

Tables 1 and 2 show in greater detail the growth and the size of the plantation industry. You will note that the total area planted at the end of 1928 was 7,067,000 acres, which is equivalent to 11,040 square miles or 105 miles square. For the sake of comparison, it may be mentioned that this is equal to the combined areas of the states of New Jersey, Delaware and Rhode Island. Since the trees are generally planted on the average 225 to the acre (estates, 150, and natives, 300), the plantations contain approximately 1,575,000,000 trees, and about 70 per cent of them are bearing. At 380 lbs. an acre the total *potential* annual yield is almost 1,200,000 long tons of crude rubber. The relative decrease in the percentage of rubber imported into the United States in 1926–28 is due to the increased production and use of "reclaimed" rubber, which amounted to about 250,000 long tons in 1929.

2. Sources of crude rubber

Rubber is obtained from the milky exudations of trees, shrubs and vines, belonging to several large botanical families which grow chiefly in the tropical zone. Some of these families and their important genera are EUPHORBIACEAE, which includes the *Hevea, Manihot* and *Micandras;* URTICACEAE, the *Ficus* and *Castilloa;* APOCYNACEAE, the *Funtumia, Landolphia* (vine rubbers), and *Clitandra* (creepers); ASCLEPIADACEAE, the *Asclepias* (milk weeds); and COMPOSITAE, *Parthenium argentatum,* (the guayule shrub). The crude or raw rubbers obtained from these different sources vary in their physical and chemical properties, some being firm and strong and others soft and weak. They all contain a hydrocarbon $(C_5H_8)_x$, "resins," etc., and their properties depend largely upon the relative amounts of these substances. The plantation rubbers and "Fine Para" contain 90–93 per cent of the hydrocarbon and 2–4 per cent of "resin," whereas other varieties may contain as low as 25 per cent of the hydrocarbon and as high as 60 per cent of "resins." The raw rubbers are obtained by coagulation of the latex with dilute acetic or formic acid, or with salts such as alum, by heating in smoke ("Fine Para"), by "spontaneous" coagulation—caused by the formation of organic acids

from bacterial action—and by evaporation on a drum or in a spray drier. Guayule rubber is obtained from the guayule shrub by crushing the woody stems and twigs and separating the woody portion by "water logging" it (3). On account of the importance and general use of plantation rubbers only such will be considered hereinafter unless mention is made otherwise.

3. Latex (4, 5, 6, 7, 8)

The latex is the milky fluid contained in microscopic tubes known as latex vessels which are found in all parts of the tree. It is under a certain turgor pressure and yet ordinarily there is no internal flow. For commerce it is obtained by tapping the trunk (9) where it is found in the cortex layer, the layer between the bark and the cambium layer. The cambium layer is very thin and lies between the cortex and the large woody inner section of the trunk, and it is through this layer that the sap travels up and down the tree. It is seen, therefore, that the latex is separate from the sap, and in fact is quite different from it. The usual method of tapping is to make an incision 1–1.5 mm. deep with a V- or U- shaped cutting tool along a slanting line three to four feet from the ground and extending one-third of the way around the trunk. This incision is then shaped in such a manner that the bottom of the V is below the bottom line of the incision, thus making a trough or channel in which the latex as it oozes out flows to the lower end, where a spout is placed to direct it into the collecting cup. The trees are tapped every other day by skilfully cutting out a very thin shaving along the lower side of the V-shaped channel. In this way the channel is lowered about one inch a month and about one foot of bark is therefore removed from the tapped section in the course of a year. The trees can be tapped when they are five to seven years old and for many years thereafter. The wounds heal and in after years the same sections can be tapped over again. The trees exhibit the phenomenon known as "wound response" and up to certain limits of tapping they give greater yields as time goes on. The latex flows for about an hour after tapping and an average tree yields about 15 cc. of latex at each tapping. Since the latex contains about 30 per

cent of its weight of raw rubber, one tree gives approximately 900 grams (2 lbs.) a year. The trees grown under the new bud-grafting system (10) produce from two to three or more times this amount. In this system, buds from high-yielding trees are grafted to one-year-old seedlings in the nursery and subsequently transplanted to the field.

The latex upon microscopical examination is found to consist of numerous minute globules suspended in a watery solution. These globules are frequently pear-shaped, are 0.0005–0.003 mm. $(0.5-3\mu)$ in diameter, and exhibit the usual Brownian movement; and each one carries a negative electrical charge (11). According to Hauser (12), they consist of a viscid interior and a firm elastic membrane which when pierced allows the contents to ooze out. Protein and resins are probably adsorbed on the outer surface. von Weimarn (13) describes latex as a polydisperse system of iso-aggregate particles with a general liquid-jelly consistency. He regards each particle as made up of smaller particles with a liquid-gelatinous interior, each one being surrounded by a layer of adsorbed protein and resins, and the larger pear-shaped particles as made up by the combination of other smaller particles of unequal size. For the most part, the isoaggregate particles are indistinguishable under the ultramicroscope. Addition of a coagulant causes the cessation of the Brownian movement, the globules coalesce and then form strings or clots (14). The globules in latex from the leaves and young twigs are smaller than those from the stems and trunk; the globules in latex from younger trees are smaller than those from older ones. The specific gravity of the fresh latex varies from 0.967 to 1.000, corresponding to 45 and to about 17 per cent of rubber respectively. So-called normal or average latex contains about 33 per cent of rubber and its specific gravity is approximately 0.983. Fresh latex is approximately neutral, its pH being 7.0–7.2 (15). In a few hours after tapping it diminishes to 6.6–6.9 and coagulation takes place. This acid condition, as already mentioned, is due to bacterial action. The amount of rubber in fresh latex varies considerably —from 15 to 60 per cent—but generally it is 20 to 45 per cent. It is highest at the beginning of a tapping period or after a rest

period and also from trees well cared for; it is higher from trees tapped as mentioned above than from those "heavily" tapped, from shallow tapping than from deep tapping, and from the roots and trunk than from the twigs. Latex can best be preserved by the addition of 2–5 per cent of concentrated ammonium hydroxide; it can also be preserved with 0.5 per cent of formalin. Ammonium hydroxide lowers the viscosity of latex. Preserved *Hevea* latex "creams" on standing for several weeks (see also p. 59). Latices from the *Manihot* and *Castilloa* cream more readily, but they contain larger rubber globules.

TABLE 3

Substances in the latex and in coagulated rubber

	IN THE LATEX	IN THE CRUDE RUBBER	PORTION OF ORIGINAL SUBSTANCES FOUND IN THE CRUDE RUBBER
	per cent	*per cent*	
Crude rubber	30 0	100.0	
Rubber hydrocarbon	28 0	92 0–94 0	
Total solids	33 0–34 0	98 8–99 7	$\frac{9}{10}$
Mineral substances (ash)	0 3–0 7	0.15–0 45	$\frac{1}{4}$
Components containing nitrogen (calculated as proteins: $6 \times \%N$)	1 0–2 0	2 5–3 5	$\frac{2}{3}$
Components soluble in acetone ("resins")	2 0(?)	2 5–3 2	?
Quebrachitol	1 0–2 0	Trace	?
Reducing sugars	0 15–0 35	—	—

When *Hevea* latex is coagulated with dilute acetic acid (1 part of glacial acetic acid to 100 parts of dry rubber) and the coagulum passed between corrugated, uneven-speed rollers, in the presence of running water, there is obtained the familiar "pale crêpe" of commerce. Sodium bisulfite is added before coagulation to prevent the color formation from enzymic action. "Smoked sheet" is prepared by passing the coagulum between even-speed rollers to squeeze out the serum, and then drying the sheet in a smoke house. "L. S." rubber ("latex sprayed") is obtained by evaporation of the latex in a spray drier (16). It contains all the solids of the latex and is a very uniform and very tough product. Drying the

latex on a heated revolving drum also gives a rubber containing all the solids in latex (Kerbosch process) (17).

Although acids coagulate latex, it is possible to make the latex definitely acid without coagulating it by adding certain protecting agents, such as the sodium salt of the reaction product obtained by condensing naphthalene and isopropyl alcohol in the presence of sulfuric acid (18). Acid latex has about the same viscosity as ammonia-preserved latex.

Table 3 gives an idea of the substances contained in the latex and in the coagulated rubber obtained therefrom.

The rubber hydrocarbon is apparently the same after coagulation as before. The protein is not necessary as a stabilizer because when it is removed the latex is still stable, and acid coagulates it as it does before (19) (20). The nature of the protein is not well understood, but it is probably a globulin. The proteins and their decomposition products remaining with the crude rubber act as accelerators of vulcanization and confer other important properties on the rubber. Analysis of the ash shows that it consists chiefly of sodium, potassium, calcium and magnesium phosphates and a small amount of sulfate and sometimes chloride. The quebrachitol ($C_6H_{11}O_5OCH_3$) is a methyl ether of inositol (a cyclic sugar) and is levo-rotatory. It has the following structure:
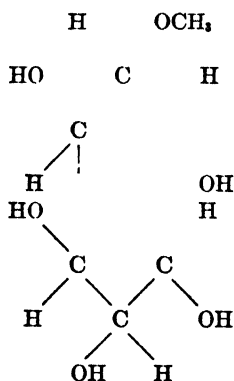
Some glucose is present among the small amount of reducing sugars, and traces of hydrogen cyanide and of acetaldehyde have

also been found in latex. Other substances found in latex, and generally included in the "resins" obtained in the "acetone extract" of crude rubber are as follows (21) (22) (The figures given in parentheses represent the per cent present in crude rubber): Oleic and linoleic (1.3), and stearic (0.15) acids which comprise about one-half of the total weight of the extract; quebrachitol (1-2), a phytosterol (0.225), a phytosterol glucoside (0.175), two liquid sterols, $C_{27}H_{42}O_3$ (0.08) and $C_{20}H_{30}O$ (0.16), a sterol ester, $C_{17}H_{32}O_2 \cdot C_{27}H_{45}$ (0.075), d-valine (0.015), n-octadecyl alcohol, a ketone, $C_{15}H_{24}O$, and a hydrocarbon, $C_{15}H_{24}$. The fatty acids play an important part in the vulcanization of rubber especially in the presence of organic accelerators, because the oxides of zinc, lead, magnesium, etc., are converted into the corresponding organic salts which are soluble in the rubber (21) (23) (24) (25) (26). The liquid sterols are powerful, naturally-occurring antioxidants and are chiefly responsible for the preservation of crude rubber (22). The amount and nature of the acetone extract also affects the "working" properties of crude rubbers and their physical properties after vulcanization.

Crude rubber can be redispersed to form an artificial latex by milling into it a hydrophilic colloid, such as glue and certain clays, and then mixing in water (27). The artificial latex has properties very similar to those of natural latex and is finding interesting commercial applications. Reclaimed rubber can also be dispersed in the same general way (28).

4. Concentration and uses of latex

During the creaming process mentioned above, the rubber hydrocarbon becomes more concentrated in the upper layer just as the fat in milk becomes more concentrated in the cream. This concentration (of preserved latex) on long standing can also be carried on by centrifuging (29), and by the addition of certain hydrophilic creaming agents, such as Irish moss, gelatin, ammonium alginate, etc. (30). These creams, when separated, are found to contain upwards of 75 per cent of rubber hydrocarbon, and this high amount approaches the calculated maximum value for close packing of spherical particles (31). The creams are

comparatively free from the water-soluble, non-rubber constituents of latex. Direct concentration of latex can be carried out by the addition of potassium hydroxide and other stabilizers such as potassium salicylate or fluoride, followed by evaporation under diminished pressure in a rotating drum (revertex process) (32). These creams and other concentrated latices are often almost butter-like in consistency, but can be readily diluted with water.

Latex is used commercially in the manufacture of tire web-cord fabric (33), gloves and inner tubes on porous forms by filtration (34), rubber-covered metal articles by electro-deposition (35), rubber articles of the outside shape of a porous form by electro-deposition (36), rubber impregnated mohair upholstery (37) and for backing the piles of rugs (38), special papers (39), etc.

Latex can be vulcanized by heating with alkali polysulfides (40).

5. Function of latex in the tree

The exact purpose of the latex is not definitely understood (41). It no doubt has some relation to the environment of the tree, that is, an ecological function (42). In some cases it may serve as a protective layer against insects, because it is known that where the latex vessels have been removed, the tree is attacked by borers. Latex occurs in some but not in all organs and therefore apparently has no indispensable function to perform for the continuance of the life of the plant; it has no influence on the development of sieve tubes nor can these be replaced by latex vessels (43). Latex contains organic materials provided by the assimilative and metabolic processes of the tree, and it may, therefore, have nutritive value. For example, it has been shown (44) that during the period of leaf-fall and new leaf-formation in March and April, "The yield per tree was very low. . . . . This variation in the amounts of rubber obtained agrees with the order of variation in the amounts of reserve starch in the bark and wood during the same months." Furthermore, in studies on the guayule shrub, Macallum (45) has found that the rubber content increases after cutting if preserved under proper conditions, increases under conditions that generally result in other plants in the storing up of

starch, no reserve food in the form of starch being laid by, and decreases during periods of extensive growth.

It should be added that the chemical forerunner of the rubber hydrocarbon is not known and that the process of its conversion to rubber is still an open question.

6. The importance of vulcanization

A good quality of crude rubber is tough, strong, resilient, elastic, and resistant to abrasion (witness its use as crêpe rubber soles), but by means of vulcanization these qualities can be enhanced greatly and can be made to hold over a much greater range of temperature (46). Crude rubber becomes soft and sticky when heated even to 100°C., and, when cooled beyond a certain point, becomes stiff and horn-like. The early raincoats manufactured before vulcanization was discovered became useless in midsummer because they tended to "run" and stick, and in winter they became unyielding like a one-piece coat of armor. Vulcanization changes all this, increases immeasurably the varieties and grades of soft rubber articles, gives the rubber its capacity to hold the shape of the mold in which it is fashioned, makes it more insoluble in organic solvents and much less absorbent of water, and increases enormously its durability. As a specific example there may be mentioned the automobile tire. The tread has most remarkable resistance to abrasion, its resilience is noteworthy, and even at the high running temperatures in midsummer, 65-80°C. (47), it keeps these qualities and its shape unchanged.

II. THE RUBBER HYDROCARBON

1. Isolation and properties

The word "rubber" may mean the crude or raw rubber, or vulcanized articles made therefrom. The word itself comes from the use of crude rubber for rubbing out pencil marks. It was recorded in this meaning in 1770 by Priestley (48), and, according to a recent article by Speter (49), it was used even a little earlier by Nairne, a maker of mathematical instruments in London. The term "India-rubber" was given to it because of the fact that it was first

brought to Europe from the land which Columbus and his contemporaries thought was India,—namely, the West Indies. The French word is "caoutchouc," and the German, "Kautschuk,"—both from the native words meaning "weeping tree" (*caa o-chu*). C. O. Weber, the "Father of the Chemistry of Rubber," used the word "polyprene" for the purified rubber hydrocarbon. This word was coined from polymer and isoprene. Some writers have used the French word for crude rubber, caoutchouc, to signify the purified rubber hydrocarbon, but its use leads to ambiguity. Since it is not known whether the rubber hydrocarbon consists of a single hydrocarbon or of a mixture of hydrocarbons, it seems best to speak of it simply as the rubber hydrocarbon.

Rubber owes its characteristic properties to its chief constituent—the rubber hydrocarbon (50). Although it has been isolated in a high state of purity, not all of its properties are well understood. Its strength, tackiness, stretch, rate of solubility (dispersibility), resilience, etc., vary with the kind and manner of physical treatment. Working it between the rolls of a rubber mill causes it to become plastic (putty-like) and at the same time to become weak, less extensible, less resilient, more tacky, more readily soluble, etc. Other methods of treatment, such as stirring in solution, and exposure to the action of light and of certain reagents, cause similar changes. This so-called "breaking down" or mastication (51) of the rubber is very important, because it is on account of this property that it is possible to mill into the rubber the necessary ingredients for vulcanization and for preparing the rubber for such an infinite variety of uses. Whether this change is entirely physical or chemical or both is not yet known. The chief constituent of rubber is, no doubt, a polymerized hydrocarbon with colloidal properties, and if it is depolymerized during the "breaking down," then there should be a corresponding increase in the chemical unsaturation per unit group. A. E. Gray and the writer (52) found, however, that, within the error of the method employed, there was no change in the unsaturation when rubber was milled for several hours in an atmosphere of carbon dioxide, although in air there was a decrease of about 2 per cent. However, if the rubber molecule is very large, as it

seems to be, then the relative change would be very small,— probably smaller than the error of the method employed.

A 10 per cent solution of unbroken-down rubber forms a solid gel, but after thorough milling of the rubber, a 10 per cent solution is of about the same viscosity as that of the solvent itself. Ultra-violet light also causes a great lowering in the viscosity of a rubber solution, and here again there is no apparent change in the chemical unsaturation (52). Heat and certain acids (e.g. trichloroaceict acid) and other substances also cause a considerable lowering in the viscosity, but in these cases the change is generally in part at least a chemical one, because there is a change in the unsaturation on account of isomerization or polycyclization (53) (see p. 115). Broken-down rubber, if left undisturbed for some time, will slowly regain part of its "nerve." It should be remarked that the more rubber is broken down in the manufacturing process, the less is the strength and other important properties of the vulcanized product made therefrom.

The rubber hydrocarbon can be obtained in a fairly pure condition by extracting the resins of the raw rubber with acetone, dissolving the extracted rubber in benzene, decanting from the insoluble material, precipitating by pouring the solution in alcohol, and repeating these last operations several times. This is Harries's well-known method (54). However, even when this process is carried out in an atmosphere of carbon dioxide, as shown by Pummerer and Burkhard (55), the hydrocarbon still contains small amounts of proteins and sugars. Fractional precipitation of a petroleum ether solution in acetone (56) gives a better product, but it also is not always free from nitrogen. Purification with methyl alcoholic potash (57) gets rid of all the nitrogen, but the last traces of the alkali are very difficult to remove. When acetone-extracted, unbroken-down crude rubber is allowed to stand in a solvent like petroleum ether, the rubber hydrocarbon slowly diffuses through the network of insoluble substances and there is thus obtained a very pure product, free from nitrogen, and analyzing $(C_5H_8)_x$. However, this method, originally due to Caspari (58), and recently used to good advantage by Feuchter (59) and by Pummerer and Miedel (60), accounts for only about

70 per cent of the hydrocarbon present, a difficultly soluble portion remaining behind.

The best and most complete method for purifying the rubber hydrocarbon is that of Pummerer and Pahl (20) by the direct use of latex. This method, which is carried out in an atmosphere of nitrogen in order to avoid any oxidation, is as follows: Preserved latex is treated with a solution of sodium hydroxide (2 per cent of the total solution) for two days at 50°C., to hydrolyze the protein, and is constantly stirred. On standing at the end of this time, creaming takes place. The lower alkaline layer is siphoned off and the treatment repeated four times. Even before the last treatment, the biuret and the ninhydrin reactions for proteins no longer show the presence of any protein. The remaining alkali present in the cream is separated by washing and finally by dialysis. The rubber hydrocarbon is then coagulated by the addition of acetone or acetic acid, extracted with acetone to remove any remaining resins, and dried in a high vacuum. The acetone extract contains practically no resins and serves chiefly as a preliminary removal of water. The product, even in thick pieces, is transparent, pale yellow in color, elastic, and not tacky. The ash content is as low as 0.077 per cent. The analytical figures agree very closely with $(C_5H_8)_x$. The earlier publications stated that the preparations were free from nitrogen. Later, however, Pummerer, Andriessen and Gündel (61) found that, although no protein was present, the samples still contained some nitrogen, 0.04–0.1 per cent, which is probably due to the presence of amines. Pummerer (62) then found that samples with less than 0.04 per cent of nitrogen can be obtained from revertex-S (see p. 60).

Cummings and Sebrell (50), using the method of Pummerer and Pahl, but changing the alkali several more times, have been able to prepare a purified rubber hydrocarbon with a nitrogen content of only 0.004–0.0096 per cent. It is protein-free, and when extracted with acetone the amount of nitrogen falls so low that it cannot be measured with accuracy by the exact method used by them,—namely, colorimetric determination with Nessler's solution.

The highly purified rubber hydrocarbon contains all the original

hydrocarbon, including the insoluble or difficultly soluble portion that is left behind in the diffusion method mentioned above. These two portions can now be separated, if desired, by means of absolute ether, the ether-soluble portion being called "sol-rubber" or alpha-rubber and the insoluble portion "gel-rubber," or beta-rubber. This, however, is not an exact separation, because even after ten days of continuous extraction a constant condition is attained where only a very small but weighable constant amount goes into the ether per day. With ether extraction the amount of gel-rubber is about 35 per cent, but with other solvents, it is lower. Both portions give similar analytical results. Sol-rubber is colorless and very elastic; gel-rubber is brownish and very

TABLE 4

Analysis of sol-rubber and gel-rubber

	CARBON	HYDROGEN
	per cent	*per cent*
Calculated for $(C_5H_8)_x$.............................	88.15	11.85
Ether-sol-rubber: Found...........................	88.00 87.98	11.94 11.90
Ether-gel-rubber: Found...........................	87.72 87.96	11.98 11.93

tough, and contains a trace of ash. The analytical figures for these two varieties are as given in table 4. When the gel-rubber is broken down on the mill in an atmosphere of carbon dioxide it becomes completely soluble in ether, and when ether solutions of sol-rubber are evaporated, after standing, traces of gel-rubber insoluble in ether are found. These are interesting points because of their bearing on the theory of a two-phase system in rubber. The breaking down may be due to disaggregation, according to Whitby (63) and Harries (64), but even this term does not fully explain what happens. Furthermore, whether sol-rubber is simply disaggregated gel-rubber, and whether gel-rubber is aggregated sol-rubber still remains to be seen.

The rubber hydrocarbon is decomposed by certain surface

molds (68). Losses in weight up to 30 per cent have been recorded, but even when 20 per cent of the rubber hydrocarbon was decomposed, the remaining rubber showed very little change in any important properties.

It is of interest to note that rubber was first analyzed by Faraday (65), who gave it the same formula used to-day. Other important contributions to the establishment of this formula, besides those just discussed, have been made by Weber (66), Gladstone and Hilbert (67), and Harries (54).

2. Crystalline rubber

Unstretched frozen rubber exists in a crystalline form as shown by x-ray studies (see p. 67) (69). Also, the rubber hydrocarbon has been obtained in crystalline form at room temperature. Pummerer and Koch (56) isolated the crystals while working with solutions containing the purified hydrocarbon prepared by fractional precipitation. Analysis showed them to have the formula $(C_5H_8)_x$. They are very sensitive to oxidation, probably on account of the relatively larger surface exposed to air as compared with that of the ordinary non-crystalline variety. They become transparent and plastic at about 60°C. and begin to melt at about 92°C. They are colorless, and show relatively little elasticity and "nerve." The crystals shown in the photomicrographs given in the original article are fully described crystallographically, showing that there are three crystalline varieties in six different crystalline formations. Since these did not appear to be modifications of the same substances, the authors concluded that "there are several chemically different substances in the sample."

3. Molecular weight and other physical properties

The molecular weight of rubber is high, as indicated by its colloidal properties. Hinrichsen and Kindscher (70) calculated it to be 3173 by the cryoscopic method in benzene solution. This is probably a good average figure according to the recorded work of the older investigators. Staudinger (71) considers the "macromolecules" of rubber to consist of 100 to 1000 C_5H_8 groups, corresponding to molecular weights of 6800 to 68,000. Very recently,

Pummerer, Nielsen and Gündel (72), using camphor as the solvent as suggested by Rast, at concentrations of 1:4 and 1:10 found molecular weights of 1100 to 1600. In menthol at a concentration of 1:50, molecular weights of 1200 to 1600 were obtained; on dilution to 1:100 the values obtained were only 520 to 620, indicating extensive dissociation. Further dilution caused no decrease. These lower figures were obtained with samples of highly purified rubber hydrocarbon prepared by different methods and with samples of both sol- and gel-rubber. The results indicate eight C_5H_8 units or a molecular weight of 544, although the experiments do not warrant the acceptance of this as an established fact as yet. The authors point out that samples of great difference in solubility show the same average molecular weight in camphor and in menthol, and that, therefore, their essential difference must lie in their different powers of aggregation. Staudinger, Asano, Bondy and Signer (73), however, criticize the results obtained with camphor and menthol, stating that these solvents, even with substances of more finite molecular weights, give figures which vary considerably with the time of heating, the amount of supercooling, etc. Purified rubber hydrocarbon from latex gave in menthol values from 363 to 1160, and in camphor, 2200, the concentration being low in each case as in Pummerer's experiments. The authors believe that only a hydrocarbon should be used as the solvent for determining the molecular weight of another hydrocarbon. Pummerer (74) has produced further evidence to support his earlier observations, but the question of the molecular size of the rubber hydrocarbon is not yet settled.

X-ray studies (69) (75) (76) (77) have shown that unstretched raw rubber produces a diagram typical of an amorphous material —that is, a single, broad, diffuse ring. As raw rubber is stretched beyond 75 per cent elongation, the x-ray diagram shows a marked change. In addition to the amorphous ring, which is always evident but decreases in intensity with increase in elongation, there appear instantaneously definite interference spots, which become sharper and more distinct the greater the stretching but retain the same positions. The entire phenomenon is reversible if the sample is not too strongly stretched, the amorphous diagram

being obtained again when the tension is released.   If, however, the rubber is stretched slowly, no interference spots appear at all (78).   When the rubber is stretched, cooled, and then released, the interferences remain unchanged.   When the stretched rubber is heated, the interferences become less intense and disappear at 60°C.   They also disappear when the stretched rubber is placed in an atmosphere of the vapor of a solvent, such as benzene. The intensity of the diffraction interferences increases in direct proportion to the percentage elongation of the stretched rubber, and this increase in intensity is explained by the continual appearance of new diffracting crystal-like individuals.   The evidence seems to support the contention that the crystals do not exist as such prior to the stretching, although rubber which has stood for some time at low temperatures and has become opaque and hard, gives a pattern of sharp, concentric rings, indicative of small crystal grains in random orientation (79).   The same results with x-rays have been obtained with both sol- and gel-rubber and with eighteen different samples of crude rubber from various parts of the world.   It is evident, therefore, that the structure of raw rubber as revealed by this method is independent of the origin or the type of rubber and is directly related to the structure of the rubber hydrocarbon (80).   Also, the stretching of rubber is a molecular, not a macroscopic, phenomenon.

X-ray studies indicate that the rubber hydrocarbon consists of long chains of isoprene groups and that these long chains probably exist as spirals which form definitely aligned fibers when the rubber is stretched.   Further work in this field will be awaited with considerable interest.

If a strip of raw rubber is stretched while warm and cooled quickly, under tension, it remains as a thin strip and is then known as "racked rubber."   If the tension is released and the racked rubber warmed, it will contract, but not to its original condition. Some of the strains are evidently "frozen in."   Repeated racking may stretch the rubber to 9,000 to 10,000 per cent elongation (81).   Such racked rubber shows a very intense x-ray diagram. If stretched or racked rubber is frozen with liquid air and then struck with a hammer, it splits into fibres.   Unstretched rubber

under these conditions shows a conchoidal fracture. Hock (82), who did this work, was also able to show the same effect with "diffusion" rubber, and, working at lower temperatures, with vulcanized rubber. He reasoned, therefore, that the fibrous structure is a property of the molecules or molecular aggregates common to all modifications.

Rubber, upon being stretched, gives off heat and becomes cold again when it is immediately allowed to return to its original position. This heating during the stretching is known as the Joule effect. Recent data show that it is directly proportional to the degree of elongation (83), just as the intensity of the x-ray diagram is also directly proportional to the degree of elongation.

van Geel and Eymers (84) have derived a relation between the double refraction and the elastic tension of rubber. The formula given by them defines double refraction as a function of the tension up to a certain limiting value of the tension, at which point a strict proportionality between double refraction and tension begins. The elongation at this limiting tension is 70 per cent, —the same elongation at which x-ray photographs begin to show fibre diagrams. It appears, therefore, that 70 per cent elongation "is a characteristic constant of pure rubber."

The specific gravity of raw rubber is 0.91–0.93; that of the pure hydrocarbon is 0.920 at $17°/4°$ (85). Racking causes a decrease in the specific gravity; freezing causes an increase. At 36–8°C., frozen rubber shows a sudden decrease in density and hardness, and an increase in transparency (86). These changes are probably the result of the fusion of a crystalline component. Other physical constants of rubber are given on p. 119.

Rubber forms colloidal solutions in benzene, gasoline, chloroform, carbon tetrachloride, carbon bisulfide, absolute ether, and similar solvents. It is precipitated from solution by alcohol, acetone, etc. Raw rubber is insoluble in water, but, on being allowed to remain in it, will absorb water up to about 25 per cent of its weight (87). Unwashed rubber, of course, absorbs more water than washed rubber on account of the presence of water-soluble components. Solutions of raw rubber in organic solvents are more or less turbid, depending in part on the amount and kind

of the non-rubber constituents and in part on the solubility of the gel-rubber portion. Gel-rubber is more soluble in the aromatic hydrocarbons (cumene is the best), and therefore the aromatic hydrocarbon solutions of purified rubber are clear, whereas the petroleum ether and absolute ether solutions are clear only when the gel-rubber has been removed or rendered soluble. All these solutions show the familiar Tyndall effect. They are optically inactive (88).

The viscosity of a rubber solution depends not only on the concentration but to a very great extent on how much the sample has been "worked." As mentioned above (p. 63), a 10 per cent solution of unbroken-down pale crêpe forms a gel, whereas a similar solution of rubber which has been heavily milled, even in an atmosphere of carbon dioxide to prevent oxidation, has about the same viscosity as the solvent itself. In addition to this change and those caused by heat, light, etc., as discussed on p. 63, it should be mentioned that when a solution of rubber is heated to boiling on the steam bath and protected from evaporation as well as from oxidation by carbon dioxide, the viscosity, which becomes less with the rise in temperature, returns to its original value upon cooling, whether the solution is cooled slowly or suddenly (55). Harries (54) had previously reported that the change was not reversible, but he did not guard against oxidation, which causes a considerable lowering. van Rossem (89) showed that oxygen causes a rapid lowering of the viscosity of a solution of rubber during heating, although no oxygen is absorbed for several hours. The oxygen apparently acts as a catalyst, since inert gases do not have this effect. Staudinger and Bondy (90) found that heat alone lowers the viscosity of a solution of rubber, but Pummerer (91) maintains that even traces of oxygen cause a considerable lowering of the viscosity. He also found that oxygen-free solutions which have been heated for a long time (twelve days) on the steam bath show a decrease in viscosity.

Whitby and Jane (93) studied the effects of small amounts of certain substances on the viscosity of solutions of cold-extracted pale crêpe and found that (1) precipitants like alcohol cause practically no change in viscosity, (2) organic acids, especially

the chlorinated acetic acids, cause a rapid lowering, (3) organic bases, such as aliphatic amines, piperidine, etc., cause a similar lowering, (4) reactants like bromine and iodine show an immediate lowering which increases with time, while tetranitromethane shows an unusually great lowering, and (5) small quantities of potassium hydroxide cause an increase but larger quantities a decrease. Spence and Kratz (94) had earlier found that trichloroacetic acid caused a considerable lowering. This substance should now, however, be classed with reactants because it also causes a change in the unsaturation (see p. 63).

When a solution of rubber in petroleum ether is allowed to form on mercury a film insufficient to cover the entire area, its thickness as given by Sheppard, Nietz and Keenan (92) is only 1.5 Å. This is very small as contrasted, for example, with a molecular film of stearic acid on water which is 21 Å. thick. It appears, therefore, that the rubber particle is of the "macromolecular" type and lies very flat under such conditions.

4. Action of heat

The pure rubber hydrocarbon softens at 130–45°C., sol-rubber at 115–30°C., and gel-rubber at 145–60°C. (20). Crystallized rubber becomes transparent and plastic at 60–2°C. and molten at about 90°C. (56). It will be recalled that the x-ray interference diagram becomes less intense and disappears at 60°C.,—the temperature at which Pummerer's crystals become plastic and isotropic.

At ordinary vulcanization temperatures, around 140°C., rubber softens and becomes plastic but there is apparently no chemical change (52). However, as the temperature rises, and especially as it approaches 270°C., not only does the rubber become semi-liquid, but it also slowly undergoes a chemical change as is noted by the definite lowering of the unsaturation (2.5 per cent in five and one-half hours at 245–65°C.) (52) (95). Heating an ethereal solution of rubber at 250°C. for many hours causes a lowering of about 20 per cent; above this temperature the change is comparatively rapid. For example, heating for 2 hours at 285°C. followed by 5 hours at 345–63°C. caused a drop of 51 per cent.

This change is only in the unsaturation, because the hydrocarbon remains as $(C_5H_8)_x$. It belongs, therefore, to a general type of isomerization and is no doubt due to internal cyclic formation,—polycyclization. This will be discussed again later (p. 117).

Heat decomposition, that is, dry distillation, of rubber has been carried out by several investigators. C. Greville Williams (96) in 1860 isolated a C_5H_8 hydrocarbon boiling at 35°C., and named it isoprene. Tyndall (97) proposed the structure of isoprene

$$CH_3$$
as $CH_2: \overset{.}{C} \cdot CH:CH_2$, and Euler (98) proved it by synthesis. Himly (99) had previously isolated a low-boiling product and a high-boiling one, 168–71°C., naming them respectively, "faradayin" and "kautschin." The latter was also called "caoutchene," and was found to be impure dipentene. Bouchardat (100) later obtained isoprene, dipentene and "heveene," $(C_{15}H_{24})$. Ipatief (101) showed that the isoprene fraction contained some trimethylethylene (b.p. 38°C.). This hydrocarbon is probably not a primary decomposition product, but is possibly formed by the partial reduction of isoprene during the heating. Harries (102), working under Emil Fischer in 1902, reinvestigated the subject by more refined methods in a vacuum of 0.25 mm. pressure. He found that the amounts of isoprene (seldom over 1 per cent) and of dipentene were small and that the chief fraction was an oil boiling at 220–60°C. More recent and more complete work in this field is that of Staudinger and Fritschi (103), who heated carefully purified rubber in a vacuum of 0.1–0.3 mm. pressure. The final temperature of the metal bath employed was 350°C. The residue, a resinous mass, amounting to 36.5 per cent, was found to be only about one-half as unsaturated as the original rubber, and was therefore a polycyclo-rubber. Fractionation of the distillate in a high vacuum, and determination of the boiling point, molecular weight, refractive index and bromine absorption of the chief constituents, showed the presence of isoprene, 3.1 per cent; dipentene, 8.8 per cent; a $C_{15}H_{24}$ hydrocarbon with two double bonds and two rings, possibly a hydronaphthalene derivative, 4.4 per cent; a $C_{15}H_{24}$ hydrocarbon containing three double

bonds and two rings, 3.8 per cent; a $C_{35}H_{40}$ hydrocarbon containing four double bonds and two rings; and higher boiling terpenes which decomposed on redistillation. No open-chain terpenes were found. The polycyclo-rubber that is formed during the course of the heating can also be decomposed if the temperature is raised to 350–400°C., but no isoprene and no dipentene are obtained (see p. 120).

Staudinger and Geiger (95) later showed that by rapid distillation at ordinary pressure and in an atmosphere of carbon dioxide almost all of the rubber can be converted into volatile products. For example, the distillate from a 500 gram sample of acetone-extracted rubber consisted of 92.8 per cent, and of this, 0.4 per cent was liquid at −80°C., 2.6 per cent boiled at 25–32°, 4.3 per cent was the isoprene fraction boiling at 32–5°, 5.8 per cent boiled at 45–150°, 23.8 per cent, the dipentene fraction, boiled at 50–70° at 12 mm., and 25.9 per cent boiled above 180° at 12 mm. The slower the distillation the greater the polycyclization, and therefore the greater the residue. One hundred grams of plantation rubber distilled slowly *in vacuo* at 300°C. in an atmosphere of carbon dioxide gave 53 grams of residue which consisted almost entirely of polycyclo-rubber.

Since it is known that a rubber-like product can be obtained by polymerizing isoprene, the question naturally arises why a greater amount of isoprene is not obtained in the dry distillation of rubber, and also whether the dipentene and the polyterpenes are primary or secondary decomposition products. Under the conditions necessary to decompose rubber, isoprene readily polymerizes to dipentene and other higher terpenes and not to a rubber-like polymer. Furthermore, the heat decomposition of hydro-rubber (see p. 103) gives no isoprene but does give methyl-

$$CH_3$$

ethylethylene, $CH_2 \cdot CH_2 \cdot \overset{\cdot}{C}:CH_2$, and in greater quantity than it gives its dimer, $C_{10}H_{20}$. Also it has been shown that isoprene at 700–50°C. is converted in part into benzene, toluene, and other aromatic substances (104). Therefore, it is likely, though not completely proven, that isoprene or its straight chain homo-

logues are obtained first and that these then polymerize or rearrange into the terpene products that are isolated.

Further light on this question is given in the most recent work in this field, that of Midgley and Henne (105). They worked with very large amounts and isolated products which ordinarily would escape notice. Pale crêpe was destructively distilled in 16-pound batches in an iron vessel at atmospheric pressure, 200 pounds in all being used. The temperature was always raised as quickly as possible to about 700°C., but no attention was paid to its control. The conditions used gave unusually large yields of isoprene—10 per cent—and this was the chief object of the work. The addition of magnesium, 850 grams to 16 pounds of rubber, did not increase the yield of isoprene or dipentene, but did increase the yield of the other products, especially the aromatic products. Zinc, iron and aluminum have a similar effect but to a smaller extent, copper is without effect, and brass behaves like iron. The products obtained are olefinic, dienic, aromatic and hydroaromatic compounds. No fully saturated compound was detected. In addition to the components separated by fractional distillation, a substantial portion of the original material polymerized, remaining as a jelly in the distilling flask. The materials lost in this way probably consisted largely of dienes.

Because of the preponderance of isoprene, dipentene and $C_{15}H_{24}$ in the products of destructive distillation, the authors hold that the single bond furthest removed from the double bonds is the most easily broken by pyrolysis. They point out that this same conclusion is also arrived at by Hurd (106) from purely theoretical considerations. Accordingly, they postulate that the rubber hydrocarbon breaks at single valences to give sections, each of which contains a given number of carbon atoms, that these points of breakage are represented by partial valences, and that the double bonds are resolved into partial valence forms. Then (a) adjacent partial valences may join to form double bonds (Thiele); (b) single partial valences six carbons apart may join to form rings; (c) any pair of partial valences may accept hydrogen, preferably those not adjacent to others; (d) partially hydrogenated aromatic compounds liberate hydrogen to yield the corresponding aromatic

compounds; and (e) partial valences not joining or not accepting hydrogen may migrate. Thus practically all of the compounds isolated can be predicted.

No myrcene, or a terpene boiling at 168-9°C., or dimethylbutadiene was found in the products of destructive distillation. With the exception of benzene, the compounds of the aromatic series obtained were probably all derived by dehydrogenation of the corresponding hydroaromatic compounds, since only those aromatic compounds were formed whose hydro-derivatives were also present. The origin of the benzene is obscure; it may have been formed by pyrolysis in locally overheated spots. The percentage yields in the distillate, except in the cases of isoprene (10 per cent) and dipentene (20 per cent) were all low, being about 0.01-0.10 per cent for the straight distillation, and 0.10-1.0 per cent with magnesium. The compounds positively identified were: 3-methyl-1-butene, 2-methyl-1-butene, isoprene, 2-methyl-2-butene, 2-methyl-2-pentene, benzene, Δ^{1}-tetrahydrotoluene, toluene, m-xylene, p-tetrahydroethyltoluene, p-ethyltoluene and dipentene. Incomplete evidence was obtained for the presence of 2-methylpentene, 3-methyl-2,4-pentadiene, 3-methylhexene, Δ^{3}-tetrahydrotoluene, Δ^{2}-tetrahydrotoluene, 2-methylheptene, thujene, $C_{10}H_{18}$ with 1 double bond and dimethyloctadiene. In the straight distillation the total amount of these substances in the distillate was 0.860 per cent, and with magnesium, 9.05 per cent.

5. Structure of the hydrocarbon

There is now no question but that, as pointed out above, the empirical formula of the rubber hydrocarbon is C_5H_8. How many of these groups make up the actual molecule, and in fact, whether the natural hydrocarbon consists of a single molecule, is not yet known. The chief chemical reaction of the rubber hydrocarbon is addition. The substance is therefore unsaturated, and a study of the addition products leads to the conclusion that the fundamental grouping is C_5H_8 (not $C_{10}H_{16}$ as formerly supposed) and that there is one double bond for each C_5H_8 group. This has recently been substantiated by measurement of the refractive
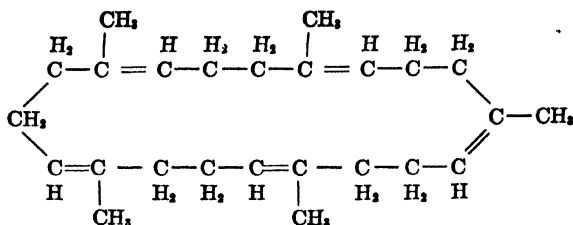
index of a film of purified rubber by Macallum and Whitby (107), and of the adsorption spectra by Scheibe and Pummerer (108). Many years ago, Gladstone and Hibbert (67), from measurements of the refractive index of purified rubber in solution, calculated that there were one and one-half double bonds to each C_5H_8 grouping, and concluded "that the main constituent of caoutchouc is a compound which for $C_{10}H_{16}$ has 3 pair of carbon atoms doubly linked." Weber also used the $C_{10}H_{16}$ nucleus, largely because of its relation to the terpenes, and Harries used the same because of his early study of rubber "diozonide."

The lowest products of the dry distillation of rubber are gases and isoprene. Since isoprene has the same empirical formula as the rubber hydrocarbon, and since it can be polymerized to rubber-like products, it is reasonable to suppose that rubber itself is a polymer of isoprene. In the course of the polymerization, one of the double bonds in each molecule of isoprene disappears, thus leaving one double bond for each C_5H_8 group. What is known as to the nature of the union of these isoprene molecules and the relative positions of the remaining double bonds was found out chiefly by Harries in his classical work on the ozonides (109). He was led to this work by observing that rubber tubing in contact with ozone rapidly perishes. Ozone adds to the double bond of an olefin forming an ozonide, and on hydrolysis such an ozonide is decomposed into aldehydes or ketones depending on the structure of the original olefin. By identification of the aldehydes or ketones, the position of the double bond can be accurately determined because the oxygen of the carbonyl groups in the decomposition products is attached to those carbon atoms which were originally united by the double bond. The ozonide formed from rubber is a glassy solid, melts at about 50°C., is very explosive, and is saturated toward bromine. The yield is a little better than 80 per cent, and analysis showed that the ozonide had the empirical formula $C_5H_8O_3$,—that is, one mol of ozone to each C_5H_8 group. Molecular weight determinations in glacial acetic acid and in methyl acetate indicated its molecular formula to be $C_{10}H_{16}O_6$. It was on the basis of this work that Harries concluded that the fundamental grouping in rubber must be $C_{10}H_{16}$.
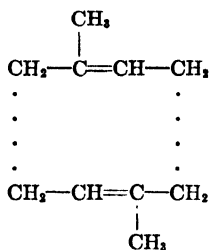
On hydrolysis the ozonide gave levulinic aldehyde, CH_3COCH_2-CH_2CHO, levulinic acid, $CH_3COCH_2CH_2COOH$, a small amount of levulinic aldehyde peroxide, and of course, the usual by-product, hydrogen peroxide. No other aldehydic or ketonic compounds were found, although the experiments were repeated many times. He therefore reasoned that the structure of the $C_{10}H_{16}$ unit must correspond to 1,5-dimethyl-1,5-cycloöctadiene,

$$HC—CH_2—CH_2—C—CH_3$$
$$\parallel \qquad\qquad\qquad \parallel$$
$$CH_3—C—CH_2—CH_2—CH$$
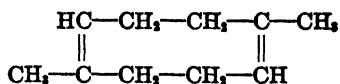
Harries assumed that this unit was polymerized by means of residual valences into the rubber hydrocarbon itself. Later, however, he found that the ozonide when dissolved in benzene gave a molecular weight 2.5 times that found in glacial acetic acid, and that its formula should therefore be written $(C_5H_8O_3)_5$ or $C_{25}H_{40}O_{15}$ (110). He also found that when alpha-isorubber, prepared by the removal of hydrogen chloride with pyridine from rubber hydrochloride, was ozonized and the ozonide hydrolyzed, not only was there obtained the customary levulinic aldehyde and acid, but also diacetylpropane, CH_3COCH_2-$CH_2CH_2COCH_3$, and other polyketones and ketonic acids. Among these were isolated a triketone with eleven carbon atoms, undecatrione, and a tetraketone with fifteen carbon atoms, pentadecatetrone. It was not difficult to account for the diacetylpropane, because in some cases the chlorine in the rubber hydrochloride was no doubt removed along with an adjacent hydrogen other than the one with which it was originally added, thus forming double bonds in different positions from and adjacent to those in the original hydrocarbon, but it was impossible to account for the presence of an eleven- and a fifteen-carbon chain compound in an eight-carbon cycle or, with the methyl groups, its corresponding ten-carbon unit. Harries, therefore, in 1914, abandoned his cycloöctadiene formula, and adopted the hypothesis, already put forth by Pickles (111) in 1910 that the C_5H_8 groups were united in a large ring, believing from his new data that the ring must contain at least 16 and probably 20 carbon atoms:

$$\begin{array}{c} \overset{CH_3}{\underset{|}{}} \quad\quad\quad \overset{CH_3}{\underset{|}{}} \\ \overset{H_2}{C}-\overset{|}{C}=\overset{H}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{|}{C}=\overset{H}{C}-\overset{H_2}{C}-\overset{H_2}{C} \end{array}$$

or better yet, as he also expressed it, without definitely stating how large the number represented by n was:

$$\begin{array}{c} CH_3 \\ | \\ CH_2-C=CH-CH_2 \\ \cdot\quad\quad\quad\quad\cdot \\ \cdot\quad\quad\quad\quad\cdot \\ \cdot\quad\quad\quad\quad\cdot \\ \cdot\quad\quad\quad\quad\cdot \\ CH_2-CH=C-CH_2 \\ | \\ CH_3 \end{array}$$

Since it is not known whether the C_5H_8 groups are united in a large ring or as a long straight chain, it is simpler to express what is known as the structure of the hydrocarbon as follows:

$$\left[\begin{array}{c} CH_3 \\ | \\ -CH_2-C=CH-CH_2- \end{array} \right]_x$$
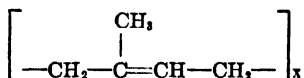
On this basis, it is now possible to indicate the action of ozone and the formation of levulinic aldehyde by hydrolysis, using only a section of the structure and inserting heavier dashes to show the bonds between the original isoprene groups:

$$\begin{array}{c} CH_3 \quad\quad\quad CH_3 \quad\quad\quad CH_3 \\ CH-CH_2-CH_2-C- \quad -CH-CH_2-CH_2-C- \quad -CH-CH_2- \quad H_2O \\ O \quad\quad O \quad\quad\quad O \quad\quad O \quad\quad\quad O \quad\quad O \\ \diagdown \quad \diagup \quad\quad \diagdown \quad \diagup \quad\quad \diagdown \quad \diagup \\ O \quad\quad\quad\quad O \quad\quad\quad\quad O \end{array}$$

$$\begin{array}{c} CH_3 \quad\quad\quad\quad CH_3 \quad\quad\quad\quad CH_3 \\ | \quad\quad\quad\quad\quad | \quad\quad\quad\quad\quad | \\ -CH_2-C + CH-CH_2-CH_2-C + CH-CH_2-CH_2-C + CH-CH_2- + H_2O_2 \\ || \quad O \quad\quad\quad\quad\quad || \quad O \quad\quad\quad\quad || \quad O \\ O \quad\quad\quad\quad\quad O \quad\quad\quad\quad\quad O \end{array}$$

Levulinic aldehyde   Levulinic aldehyde
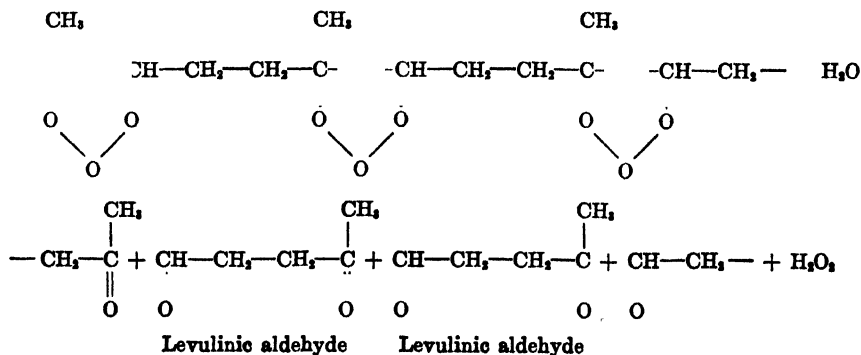
The levulinic acid always isolated along with the aldehyde is probably formed by the direct breaking up of the ozonide or by the oxidation of the aldehyde with the hydrogen peroxide.

More recent work with ozone, potassium permanganate and hydrogen peroxide has substantiated Harries's work, and, in general, his ideas. Geiger in Staudinger's laboratory (112) has found that ozone gives a mixture of acids containing one that appears to be a dicarboxylic acid with at least 30 carbon atoms in the molecule, as shown by titration. Permanganate oxidation gives acetic acid, succinic acid, levulinic acid, an acid with the formula $C_{13}H_{18}O_7$ and acids of higher molecular weight. The work of Robertson and Mair, discussed in detail on p. 99, also shows the complexity of the rubber molecule and indicates that the size of the simplest rubber molecule or aggregate is not less than $(C_5H_8)_8$.

The chemical structure of the unit group of rubber is fairly well established, but the size of the molecule, whether there are one or many molecules, whether the unit groups are united in a long chain with free valences at the ends or whether they are united in a large ring, are questions unanswered as yet. Staudinger (113) holds to the long chain hypothesis and Pummerer to the large ring hypothesis. The most recent publication up to this writing is that of Pummerer (114), in which he gives chemical evidence, based on iodine and oxygen absorption against the long open chain with free end valences.

The acceptance of the theory that the rubber hydrocarbon consists of a large ring was difficult even a few years ago, because rings of more than nine carbon atoms were unknown. However, Ruzicka and his students (115) have prepared much larger rings, one of them consisting of thirty carbons, $C_{30}H_{60}$. This is very close in size to the ring for rubber postulated by Ostromislenski (116) from his study of polyvinyl chloride and bromide ("cauprene chloride" and "cauprene bromide"),—namely, one of thirty-two carbons. Much of the recent work as already set forth has also indicated a structure corresponding to eight isoprene groups. For the sake of comparison, it might be mentioned that the compound having the largest known ring structure found in nature is cive-

tone, an unsaturated cyclic ketone with seventeen carbons in the ring (117). Other interesting hydrocarbons of high molecular weight are the yellow hydrocarbon carotin, $C_{40}H_{56}$ (M. W. 536); the compound, $C_{43}H_{88}$ (M.W. 604) found in petrolatum wax (118), and the synthetic dimyricyl or hexacontane, $C_{60}H_{122}$ (M.W. 843).

It has been known for some time that isoprene can be polymerized to a rubber-like product in the presence of metallic sodium (119), but there has been no experimental evidence for the mechanism of the reaction. Such evidence is now provided in the excellent work of Midgley and Henne (120), who placed chips of metallic potassium in contact with isoprene and then slowly added ethyl alcohol. A good yield of a light yellow oil resulted, which upon analysis proved to be a mixture of 2,6-, 2,7-, and 3,6-dimethyl-2,6-octadienes. These isomers are the three possible dihydro dimers of isoprene resulting from a junction at the 1,4-, the 4,4- and the 1,1-carbon atoms, respectively, and the addition of hydrogen to the 1,8-positions of each dimer. No trace of a compound of cyclic nature was detected.

These results help to prove that the synthetic rubber produced by contact of isoprene with the alkali metals is a long chain or large ring formed of isoprene units linked together by means of their 1 and 4 carbon atoms. The methyl groups would not necessarily be in regular order as they probably are in natural rubber. The structural formulas of isoprene and of the three dimethyloctadienes are given below, and also a possible skeleton structure of a section of a synthetic rubber chain (121). The numbers are the same in all cases, and the junction of the isoprene units is indicated by a longer bond. If such a synthetic rubber were ozonized, it can be seen that the decomposition products would be levulinic aldehyde, succinic aldehyde (or acid), and acetonylacetone. As a matter of fact, these are the products actually obtained, although the proportions vary considerably, levulinic aldehyde being the greatest in amount (122).

$$CH_2 : C \cdot CH : CH_2 \qquad CH_3 \cdot C : CH \cdot CH_2 \longrightarrow CH_2 \cdot C : CH \cdot CH_3$$

with methyl groups (CH₃) above positions 2.

| 1 | 2 | 3 | 4 | | 1 | 2 | 3 | 4 | | 1 | 2 | 3 | 4 |

Isoprene   2,6-Dimethyl-2,6-octadiene

$$CH_3 \cdot C : CH \cdot CH_2 \longrightarrow CH_2 \cdot CH : C \cdot CH_3 \qquad CH_3 \cdot CH : C \cdot CH_2 \longrightarrow CH_2 \cdot C : CH \cdot CH_3$$

| 1 | 2 | 3 | 4 | | 4 | 3 | 2 | 1 | | 4 | 3 | 2 | 1 | | 1 | 2 | 3 | 4 |

2,7-Dimethyl-2,6-octadiene   3,6-Dimethyl-2,6-octadiene

$$\longrightarrow C-C=C-C \longrightarrow C-C=C-C \longrightarrow C-C=C-C \longrightarrow C-C=C-C \longrightarrow$$

| 1 | 2 | 3 | 4 | | 1 | 2 | 3 | 4 | | 4 | 3 | 2 | 1 | | 1 | 2 | 3 | 4 |

Section of possible chain in synthetic rubber
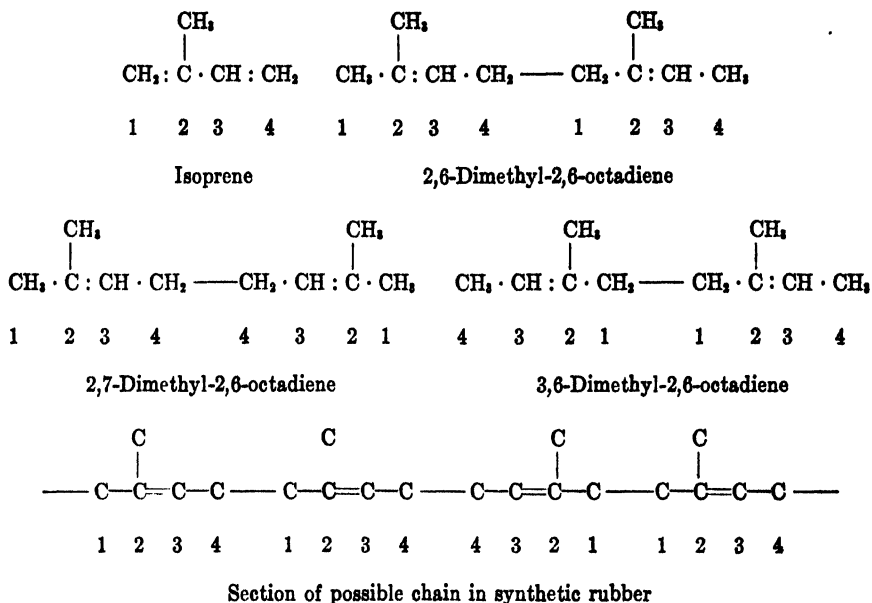
III. CHEMICAL REACTIONS AND DERIVATIVES

1. Introduction

As already mentioned, the chief chemical reaction of the rubber hydrocarbon is addition, and a study of the addition products leads to the conclusion that there is one double bond for each C_5H_8 group. Practically all of the addition reactions take place at room temperature or below, sulfur alone adding completely only at comparatively high temperatures. Accordingly, it seems most likely that there is no change in the position of the double bond during the reactions. Generally, as would be expected, the best results are obtained in solution because the reaction can then be regulated more readily. Solution may, however, have an even more important effect. Some of the addition reactions only go on or at least only go to completion when the amount of rubber hydrocarbon present corresponds to a 1 per cent solution or less. This is significant because the reactions at this dilution may possibly be linked up with the change in the molecular or "particle" size of the rubber hydrocarbon found in the determina-

tion of the molecular weight as discussed above (p. 66), but these facts are all too new and incomplete for the drawing of any general conclusions.   Whether the difference in reactivity is due to dissociation, disaggregation, or depolymerization, or something else, the fact remains that a definite change takes place, and some reactions can be carried to completion only under such conditions and apparently not otherwise.   Mastication and higher temperatures sometimes bring about the same or similar conditions of reactivity (52).

The addition products are amorphous substances of high, undetermined molecular weight.   Some are soluble in the same solvents as rubber, some in acetone, alcohol and glacial acetic acid, and some in water or aqueous alkalies; some are insoluble in all solvents tried.   When they do dissolve they form colloidal solutions. Some are unstable and some are remarkably stable.   Some are white or colorless, some are yellow or brown.   All these general properties belong not only to the immediate addition products but to the derivatives prepared from them as well.   Since they do not crystallize and cannot be distilled without decomposition, they are difficult to purify, but when purified as much as possible, they show a definite chemical composition.   On this account it is assumed that the rubber hydrocarbon from which they are prepared is a chemical individual, or consists of complexes made up of this chemical individual, such complexes acting like a chemical individual.

In discussing the derivatives themselves, greater emphasis will be laid upon the more recent work and upon the more significant properties of the older and better known derivatives which are already rather fully described in the general text-books on rubber. The C_5H_8 group will be used as the basis of nomenclature instead of $C_{10}H_{16}$.   This will create scarcely any confusion because so few names based on the old system were well-known.   Under this newer system, the older name, rubber tetrabromide, becomes rubber dibromide or simply rubber bromide; rubber dihydrochloride and dihydrobromide become rubber hydrochloride and hydrobromide, respectively.   The number of derivatives of rubber is comparatively small, and it is believed that all the known ones

that have been substantiated by their properties and analyses are included herein. The order of presentation is by classes and somewhat in historical sequence.

2. The halogen products and their derivatives

The halogens all react with the rubber hydrocarbon. Chlorine ordinarily gives a white, fibrous product in which substitution as well as addition has taken place. Substitution is the chief reaction in the early stages, as shown by McGavack (123) in a study of the effluent gases by an ingenious use of flow-meters. The product is soluble in benzene, chloroform and acetone, and these solutions upon evaporation leave a rather tough, transparent film. Chlorinated rubber is a mixture containing about 65 per cent of chlorine with the approximate formula $(C_{10}H_{13}Cl_7)_x$, and has, therefore, been spoken of as the "heptachloride." It is remarkably resistant to the action of concentrated sulfuric, nitric and chromic acids even at 100°C. It slowly decomposes, especially in sunlight, giving off hydrogen chloride.

Ostromislenski (116) states that when a 9 per cent solution of chlorine in carbon tetrachloride, containing the theoretical amount of chlorine, is added to an 18 per cent solution of extracted Para rubber in the same solvent at 0°C., there is formed rubber dichloride. It was purified by precipitation from acetone solution and analyzed for chlorine. The result was very close to the theory. He assumed it had a molecular weight corresponding to that of cauprene chloride (see p. 116), and, therefore, formulated it as a compound having eight isoprene residues, $C_{32}H_{40}(CH_3)_8Cl_{16}$.

Bromine acts like chlorine, substituting as well as adding, but in cold, very dilute solutions it gives the addition product $(C_5H_8Br_2)_x$. The formula was formerly written $C_{10}H_{16}Br_4$, and the compound was known as "rubber tetrabromide" (124). When properly prepared, it is a white, amorphous solid, which swells in some solvents but dissolves in only a very few, such as the simple halogenated hydrocarbons. If it is allowed to stand for some time as a dry powder, it then becomes practically insoluble in all solvents. This phenomenon is characteristic of a number of

rubber derivatives. Rubber bromide contains 70.13 per cent of bromine and is stable for many months under ordinary laboratory conditions, but on being heated it slowly evolves hydrogen bromide. It is not appreciably attacked at ordinary temperatures by hydrochloric, nitric, sulfuric and chromic acids. Its formation has been employed for some time for estimating the rubber hydrocarbon, either directly by isolation of the solid product (125) or more recently indirectly by determining the amount of bromine used (126) (127).

Weber (124) states that the action of boiling alcoholic sodium hydroxide upon rubber bromide is "surprisingly slight," but sodium ethylate has "a more pronounced effect." At 120°C., during 10 hours, a solution of sodium ethylate removed all but 13.38 per cent of the bromine. The resulting product weighed more than calculated from the loss of bromine, and he therefore concluded that some of the bromine atoms must have been replaced with ethoxyl groups. Hinrichsen, Quensell and Kindscher (128) stated that they could not remove all the bromine, and Kirchhof (129) found that he could not go lower than 4.5 per cent of bromine, even when he heated the rubber bromide successively with metallic calcium and alcohol, and with aniline, up to 190°C. under pressure. He also found that after such drastic treatment as heating with a mixture of metallic sodium and sodium ethylate in xylene for four hours at 150–60°C., there still remained about 9 per cent of bromine.

Iodine gives various unstable products of no definite composition, sometimes containing oxygen in addition to iodine (130). Iodine chloride has recently been used by Kemp (131) in a modified Wijs solution for estimating the rubber hydrocarbon. The method is not very difficult to carry out and the results are accurate within 0.5 per cent. A. E. Gray, in collaboration with the writer, isolated the products formed under two different conditions and found that the iodine chloride probably adds as such (see table 5). The products had apparently decomposed partially during the purification.

In 1900, C. O. Weber (132) showed that rubber "tetrabromide" and melted phenol react with the evolution of hydrogen bromide and the formation of a brownish compound, $C_{34}H_{36}O_4$, for which he

obtained excellent analyses. He considered it to be an ether and named it "tetroxyphenyl-polyprene," $C_{10}H_{16}(O \cdot C_6H_4)_4$. Other phenols reacted similarly; thiophenol gave a different reaction although hydrogen bromide was evolved, and phenol ethers such as anisole did not react at all. The phenol product was found to form dark brown solutions in alcohol, acetone, ether, ethyl acetate and aqueous alkalies, and to be insoluble in benzene, chloroform, carbon bisulfide, turpentine and petroleum ether. Since there was no reaction of the rubber tetrabromide with anisole, even though it dissolved in alkalies, he decided that "this is almost conclusive evidence that it is the hydroxyl hydrogen of the phenol which forms the point of attack in the reaction in question, and

TABLE 5

Analysis of the product formed by the action of iodine chloride on the rubber hydrocarbon

	IODINE	CHLORINE
	per cent	*per cent*
Found: Preparation No. 1............................	54.92	11.43
" " No. 2...........................	57.05	7.14
Calculated for C_5H_8ICl............................	55.02	15.39

These results have not been published previously

this fact is at the same time the reason why, in the above formula, the oxygen appears as ether oxygen and not as hydroxyl oxygen." Recently, Fisher, H. Gray and McColm (133) repeated Weber's work and verified it, but found that the phenol product could easily be methylated with dimethyl sulfate in the presence of alkali at the ordinary temperature. The methylated product is soluble in benzene and insoluble in aqueous alkalies. These facts show that the phenol groups contain free hydroxyl groups, and that the linkage between the rubber carbon and the phenol is at the ring, presumably in the para position. The reaction, using C_5H_8 as the fundamental group, could be represented as follows:

$$
\begin{array}{c}
CH_3 \\
| \\
-CH_2 \cdot C \cdot CH \cdot CH_2 \\
| \quad | \\
Br \quad Br
\end{array}
\quad + 2x\ C_6H_5OH \qquad
\begin{array}{c}
CH_3 \\
| \\
-CH_2 \cdot C \cdot CH \cdot CH_2- \\
\end{array}
\quad + 2x\ HBr
$$

OH OH
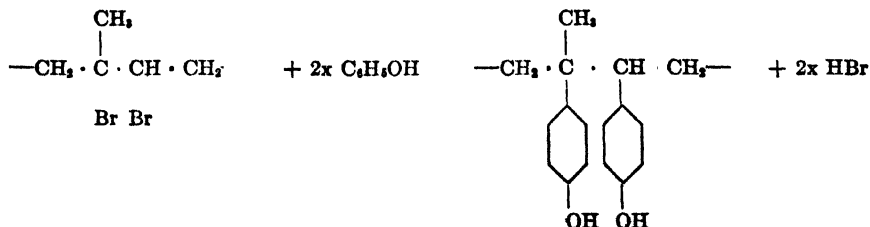
The product is therefore rubber di(hydroxyphenyl) or di(hydroxy-phenyl)-hydrorubber and the methylated product, given below, is rubber di(methoxyphenyl) or di(methoxyphenyl)-hydrorubber.
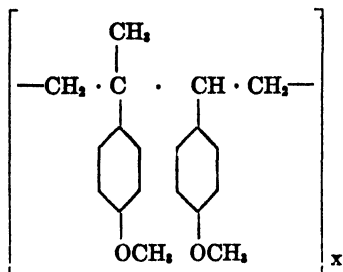
Weber's yields of the phenol product were all approximately 50 per cent. The author's yields were 65–77 per cent, even when aluminum chloride or zinc chloride was added, but became practically quantitative when anhydrous ferric chloride was used. The reaction may be like the Friedel-Crafts reaction. The yields of the methylated product are almost quantitative. The latter gave no depression of the freezing point in benzene. This is of special interest, because here we have a substance still showing colloidal properties even though it is the result of three successive reactions from rubber. The original rubber grouping therefore is probably a large colloidal molecule, a "eucolloid" as termed by Staudinger (71).

More recently Geiger (134), a former student of Staudinger, has published two excellent papers extending and elaborating this work considerably. He gives detailed results with phenol, o-cresol, resorcinol and pyrogallol, using ferric chloride as the catalyst. He also found that in the presence of ferric chloride the phenol ethers reacted like phenol itself. Anisole, for example, gave in one step the same methylated product described above. Fisher, Gray and McColm reported its melting point as 151–6°C. (corr.) and Geiger, 150–60°C. Such a verification of a physical property of a substance of this type prepared in two different ways is of considerable interest. Phenetole and methyl α-naphthyl ether reacted similarly. Furthermore, by means of benzoyl

chloride and alkali he formed the benzoates of the phenol product, $[C_5H_8(C_6H_4 \cdot O \cdot CO \cdot C_6H_5)_2]_x$ and of the o-cresol and the resorcinol products. Such of these compounds as were tested showed no depression of the freezing point in benzene solution. The phenol product and its benzoate were examined with x-rays, but only an "amorphous" ring was obtained in each case. In the second paper Geiger reported the coupling of some of these phenol products with diazotized aromatic amines (see also (135)). The reaction in each case went smoothly and rapidly at temperatures around 0°C., indicating that the coupling was similar to the usual azo dye formation. The products are colored brown to greenish-black, and are generally soluble in toluene and insoluble in petroleum ether, this difference in solubilities offering a means of purification by precipitation. They have very high molecular weights, probably over 4000, and x-ray examination gives "amorphous" rings. The phenol and resorcinol products were used chiefly, and they were coupled with such amines as aniline, p-nitroaniline, and benzidine; also with sulfanilic acid and naphthionic acid. The coupled products made from the two acids are readily soluble in aqueous alkalies, and from their red-brown alkaline solutions they can be precipitated with acids or salted out as the alkali salt. In dilute solutions they behave as indicators for acids and bases. The other products are difficulty soluble or are insoluble in alkali. All the products were not completely analyzed, but those that were have one diazo-grouping for each phenyl group. Since hydrorubber, the parent hydrocarbon, is so very unreactive, it is assumed that the coupling takes place on the phenyl groups and probably adjacent to the hydroxyl groups, as follows:
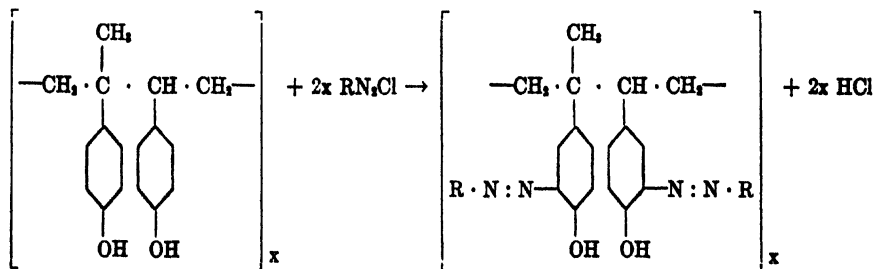
The reaction mixture of rubber bromide and phenol is always of a characteristic purplish color. The bromides of gutta-percha and of various isomerized rubbers give somewhat different colors, and Kirchhof (136) has used these color reactions as laboratory tests to distinguish these substances.

One other type of derivative has been prepared from rubber dibromide,—that is, phosphonium salts. Staudinger, Geiger and Reuss (137) have found that triphenylphosphine and triethylphosphine react with the dibromide as they do with ordinary alkyl halides. The reaction is not complete, however, since some of the bromine goes off as hydrogen bromide and analyses show that there is even less than one phosphorus group for each C_5H_8 group. The product behaves like a saturated compound, and therefore the loss of hydrogen bromide must result in internal ring formation. The position of the ring closure is not known, and for this reason the product is best represented in skeleton formation, a dotted line being used to indicate the probable position of the lost atom of bromine, and nothing being given to show where the hydrogen atom is lost:

$$
\left[\begin{array}{c} CH_3 \\ | \\ -CH_2 \cdot C \cdot CH \cdot CH_2- \\ | \quad | \\ Br \quad Br \end{array}\right]_x + x\ P(C_2H_5)_3 \rightarrow \left[\begin{array}{c} C \\ | \\ -C \cdot C \cdot C \cdot C- \\ \vdots \quad | \\ \vdots \quad P(C_2H_5)_3 \\ \vdots \quad | \\ Br \end{array}\right]_x + x\ HBr
$$
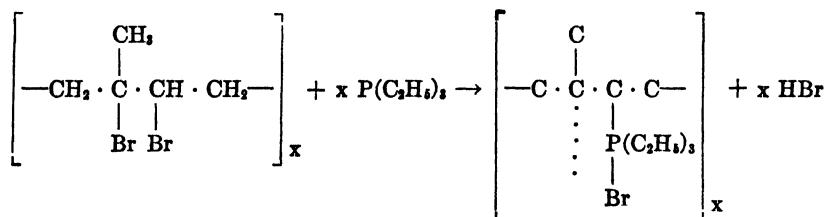
The products are insoluble in benzene, chloroform, etc., but the triphenylphosphonium compound is soluble in alcohol and ether and slightly soluble in water, and the triethylphosphonium compound is fairly soluble in water. The water solution of the latter is neutral in reaction, indicating that no hydrolysis takes place. The substance is strongly dissociated in water but is not dialyzable. In higher concentrations, the solutions are very viscous! The solid form is elastic, like rubber. With bromine they give difficulty soluble perbromides. In methylene chloride solution, the triphenyl compound gave no rise in the boiling point, and

therefore it must have a high molecular weight. These are very interesting substances, and their properties show very clearly the complex nature of the rubber molecule. Staudinger believes these reactions substantiate the theory that the rubber hydrocarbon reacts with normal valences.

3. The hydrohalides and their derivatives

Hydrogen chloride, hydrogen bromide and hydrogen iodide add to rubber to form definite addition products: $(C_5H_9Cl)_x$ (138), $(C_5H_9Br)_x$ (139) and $(C_5H_9I)_x$ (139). The reactions are usually carried out in chloroform solution, and the products precipitated with absolute alcohol. The yields of the first two are practically quantitative. In order to obtain a complete reaction, however, it is necessary to let the solution saturated with the dry hydrogen halide stand for at least twelve hours. The rubber hydrocarbon in solution also takes up hydrogen chloride slowly from concentrated hydrochloric acid. After forty-eight hours on the steam bath, a sample was found to contain 2.6 per cent of chlorine (140). The rubber hydrochloride apparently cannot be purified from unreacted rubber. The hydrohalides are white when first precipitated, but the hydrobromide and hydroiodide turn brown or black on standing because of decomposition. The hydrochloride is at first somewhat elastic, but soon becomes hard and somewhat crumbly. Its solutions, like those of chlorinated rubber, upon evaporation leave tough, transparent films, not as harsh as those of chlorinated rubber. Harries and his students have done considerable work on the hydrochloride, in the study not only of its preparation, but also of its properties. On continued purification by dissolving and reprecipitating it, hydrogen chloride splits off, and on heating it also loses hydrogen chloride. In five days at 100°C. in a vacuum it loses one-third of its chlorine as hydrogen chloride, and in twenty days, two-thirds. Heating with pyridine under pressure for 20 hours at 130°C. removes all of the chlorine as hydrogen chloride and forms "alpha-isorubber." This isorubber is softer and less elastic than natural rubber. Analysis shows $(C_5H_8)_x$, and analysis of the hydrochloride, hydroiodide and ozonide formed from it show, as in the original

rubber, that there is one double bond for each C_5H_8 group. The hydrochloride, when heated with pyridine under pressure, gave "beta-isorubber," which was more difficult to purify because it did not precipitate readily with alcohol. According to the analysis, it was probably somewhat oxidized, and the chlorine of its hydrochloride was low. Harries did a great deal of fine work on the ozonide of the alpha-isorubber and its hydrolytic products in an effort to elucidate further the structure of the original rubber hydrocarbon. In order to understand his work, the following theoretical possibilities are sketched as structural formulas using a five-carbon section. The original position of the chlorine has not been proved but it is placed on the tertiary carbon atom according to analogous cases (Markonikof's rule).

$$\begin{array}{ccc}
CH_3 & & CH_3 \\
| & & | \\
-CH_2 \cdot C{=}CH \cdot CH_2{-} & HCl & -CH_2 \cdot C \cdot CH_2 \cdot CH_2{-} \\
& & | \\
& & Cl
\end{array}$$

$$\begin{array}{c}
CH_3 \\
| \\
-CH_2 \cdot C{=}CH \cdot CH_2{-} \\
(1) \\
CH_3 \\
| \\
-CH{=}C \cdot CH_2 \cdot CH_2{-} \\
(2) \\
CH_2 \\
|| \\
-CH_2 \cdot C \cdot CH_2 \cdot CH_2{-} \\
(3)
\end{array}$$

Pyridine
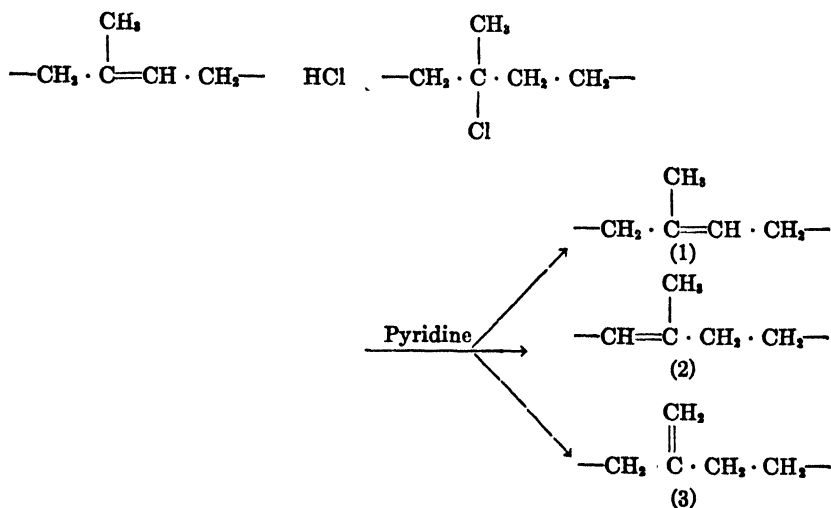
Comparison with the scheme of decomposition of natural rubber on p. 78 shows that if all the reaction went like (1), ozonization and hydrolysis would yield only levulinic aldehyde and levulinic acid as with natural rubber; if according to (2) or combinations of (1) and (2), polyketones containing the CH_3CO group would result, such as diacetyl propane, $CH_3COCH_2CH_2CH_2COCH_3$, which was actually isolated in fairly large quantities; if according to (3), then long straight chain polyketones would be formed in

addition to formaldehyde or formic acid. Undecatrione and pentadecatetrone were isolated as already mentioned (p. 77), and a great deal of formic acid was obtained. Large amounts of levulinic aldehyde and levulinic acid were also obtained, and in addition to these and the other substances given above, there were isolated succinic acid and a keto dibasic acid,—namely, hydrochelidonic acid, $HOOC \cdot CH_2CH_2COCH_2CH_2 \cdot COOH$. The formation of all these substances is therefore readily explained and involves nothing "irregular."

The rubber hydrochloride and the rubber hydrobromide have provisional structural formulas which make them an inviting field for the synthetic organic chemist. On paper many reactions for the preparation of a great variety of derivatives can be very easily outlined. But their low solubility, the very limited number of solvents available and the type of these solvents, together with their instability and their colloidal properties, all tend to make laboratory barriers which offer very considerable difficulties.

Harries, evidently in an effort to reduce the rubber hydrochloride and thus prepare hydrorubber, tried the action of zinc dust on it in ethylene chloride solution saturated with hydrogen chloride. He succeeded in removing the chlorine, but the product was somewhat unsaturated. The analytical figures for carbon and hydrogen were not very concordant but averaged pretty well for $C_{10}H_{18}$. On the C_{10}-basis this appeared to be a "dihydride," and he named it "alpha-hydrorubber" (141). But Staudinger and Widmer (85), in repeating this work, found that the chlorine-free product analyzed very well for $(C_5H_8)_x$. It is a white, hard, brittle, thermoplastic substance which is a little less than half as unsaturated as the original rubber hydrocarbon. The same or a similar substance can also be obtained from rubber hydrobromide. The disappearance of the other double bonds is most satisfactorily explained at present by polycyclic formation. These substances are representative of a series of products formed by polycyclization which will be discussed in a later section (p. 115).

Alkyl derivatives of hydrorubber have also been prepared from the hydrohalides, by Staudinger and Widmer (142). The method

comprises the double decomposition between the rubber hydro-halide and zinc methyl or zinc ethyl at low temperature. The reaction may be formulated (without balancing) as follows:

$$
\left[\begin{array}{c} CH_3 \\ | \\ -CH_2 \cdot C \cdot CH_2 \cdot CH_2- \\ | \\ Cl \end{array}\right]_x \xrightarrow{\ Zn\ (C_2H_5)_2\ } \left[\begin{array}{c} CH_3 \\ | \\ -CH_2 \cdot C \cdot CH_2 \cdot CH_2- \\ | \\ C_2H_5 \end{array}\right]_x + ZnCl_2
$$
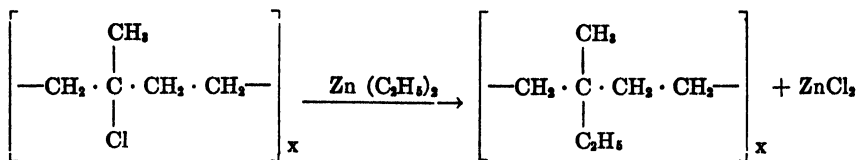
Benzene or toluene solutions were used. The hydrobromide reacted more vigorously than the hydrochloride and even at low temperatures ($-20°C$.) not only was some hydrogen bromide given off but methane or ethane was also evolved. At room temperature and higher, considerable amounts of methane or ethane were obtained. The ethyl compound was best prepared from rubber hydrochloride at $0°C$. during 3–4 days. On account of the loss of a small amount of ethane the analytical figures are slightly low. The product however does not have unsaturated properties because it is stable toward bromine, cold and warm nitric acid, and potassium permanganate. The authors believe that the small amount of unsaturation as indicated by the analyses consists of internal ring formation. The products may be con-sidered as chemical derivatives of hydrorubber. Like hydro-rubber, ethyl hydrorubber forms colloidal solutions in benzene and chloroform, and in ether, and is insoluble in alcohol and acetone. It gives no depression of the freezing point in benzene. Dry distillation of small samples gave olefins which could not be properly purified. The methyl hydrorubber was prepared similarly, but the methane formed was somewhat larger in amount than the ethane formed in the preparation of the ethyl compound. It was therefore not as pure, although the analyses were very comparable. Otherwise its properties are practically the same. Zinc ethyl does not react with rubber itself.

4. Sulfur, sulfur chloride, selenium, and selenium oxychloride

The chemical addition of sulfur is connected with the one great process of the rubber industry—vulcanization. Ordinary

soft vulcanized rubbers, such as automobile inner tubes and rubber bands, contain from 1.5 to 5 per cent of chemically combined sulfur, and ordinary hard rubber contains 25–30 per cent of combined sulfur. Practically no products are manufactured containing any intermediate amounts. Completely sulfurized rubber—that is, rubber that has had all the double bonds saturated with sulfur as in $(C_5H_8S)_x$—can be prepared by heating rubber with an excess of the theoretical amount of sulfur for many hours to 140–60°C.(143). It contains 32.00 per cent of sulfur, which is in accord with the theory. It can be obtained pure as a brown, insoluble powder by heating a cumene solution of purified rubber and a large excess of sulfur for several hours at 170°C.(144). Sulfur does not add at all, or certainly not to any perceptible extent, at room temperature. Under the influence of certain so-called "ultra-accelerators," after standing for several months, rubber may contain 0.5–0.7 per cent of chemically combined sulfur and be vulcanized (145). Practically all vulcanizations are carried on at 110–60°C., chiefly at 130–45°C.; higher temperatures are sometimes used for hard rubber. Sulfur is soluble in crude rubber and in vulcanized rubber (146). The "free" or uncombined sulfur can be removed from vulcanized rubber by extraction with acetone. When the extracted vulcanized rubber is treated with bromine (147) or iodine chloride (148), the amount that adds in each case is equivalent to the amount of sulfur that would be taken up to form the saturated compound $(C_5H_8S)_x$. No one as yet has ever isolated any rubber sulfide from ordinary vulcanized rubber; nor does incorporating purified rubber sulfide in crude rubber and then heating the mixture give a product resembling vulcanized rubber in any way. Perhaps the right method of doing this has not yet been found. So far, a true explanation of what constitutes vulcanization is still lacking (149).

The temperature rise during ordinary vulcanization of soft rubber goods is small (150). Furthermore, on account of the comparative thinness of the average articles manufactured, the heat from the reaction is rapidly conducted away and scarcely need be considered. In the manufacture of hard rubber, the case

is different. Sometimes in vulcanizing thick articles such as bowling balls, the temperature rise in the center is very great, and the heat does not disseminate quickly because rubber is a poor conductor. Violent explosions have occurred when the external heating, especially the initial rise or "stepping up," has not been regulated properly. The internal temperatures under such conditions may reach 250°C. or higher, and much H_2S is formed. If mixtures of rubber containing the seldom-used amounts of sulfur, 8–16 per cent, be heated in bulk, they too show a similar rise after the reaction sets in, and the products instead of being soft, resilient and elastic, are rather hard and thermoplastic, somewhat like a low-softening gutta-percha or a highly resinous gum such as pontianac. Kemp (151), who prepared these products, showed how they differed from ordinary vulcanized rubber, not only in these properties but also in their solubility in benzene and, according to a personal remark to the writer, in their being about half as unsaturated as the original rubber.

Sulfur monochloride in small proportions at ordinary temperatures also vulcanizes rubber. It is used in the so-called "acid" or "vapor cure" process for manufacturing rubber gloves, toy balloons, dental dam, etc. The method can be used only with thin sheets, because with thick sheets the outside becomes over-vulcanized and hard before the reagent can penetrate into the interior. When an excess of the theoretical amount for saturating each double bond is used, there is obtained, according to Weber (152), $(C_5H_8SCl)_x$, or as expressed by him, $C_{10}H_{16}S_2Cl_2$. According to Hinrichsen and Kindscher (144), only half of this amount of sulfur monochloride is added; in other words, the product is $(C_{10}H_{16})_2S_2Cl_2$ or $(C_{10}H_{16}SCl)_x$; and Bernstein (153) claims to have verified this. Weber gives a complete elemental analysis which agrees very well with the theoretical calculations for his formula. The theory for sulfur in this compound is 23.62 per cent. Hinrichsen and Kindscher isolated several products which ranged from 15.58 to 28.37 per cent of sulfur, and they then determined indirectly how much sulfur chloride had been used up, by analyzing the supernatant liquid after the precipitate had formed. Three out of eight experiments checked the formation of the prod-

uct mentioned above,—namely, $(C_{10}H_{16})_2S_2Cl_2$ or $(C_{10}H_{16}SCl)_x$. Bernstein's products contained 21.35, 28.00 and 34.68 per cent of sulfur. He also analyzed for chlorine, the respective results being 28.00, 26.30 and 23.28 per cent, while this theory calls for 26.19 per cent. He finally used only a slight excess of the reagent in dilute solutions, isolated the products, and showed that the per cent of chlorine and sulfur was close to the values required by the formula arrived at indirectly by Hinrichsen and Kindscher. Later, Kirchhof (154) passed the vapors of sulfur chloride into solutions of rubber and analyzed the effluent gases. From these results, the compounds formed were found to be midway between the two types. The sulfur content of the isolated products,

TABLE 6

Analysis of the product formed by the action of sulfur chloride on rubber

	CALCU- LATED FOR $C_{10}H_{16}SCl_2$	FOUND	CALCU- LATED FOR $C_{10}H_{16}S_2Cl_2$	WEBER'S RESULTS
	per cent	per cent	per cent	per cent
Carbon..............................	50.42	47.96	44.28	43.61, 43.51
Hydrogen.................	6.72	5.76	5.90	6.21, 6.14
Sulfur..............................	13.42	14.83	23.62	23.88, 23.81
Chlorine............................	29 50	29.53	26.19	25.97, 26.11

however, varied considerably, the lowest figure being above that for the "half" addition and the highest rather close to that of Weber's compound. He stated that Weber's compound was probably formed first and then partially decomposed.

After the lapse of many years, Meyer and Mark (155) took up the study of this reaction and compared it with the now familiar action of sulfur chloride on ethylene,—the "mustard gas" reaction. In this case an atom of sulfur separates as indicated in the following equation:

$$2 \ CH_2 : CH_2 + S_2Cl_2 \rightarrow (CH_2Cl \cdot CH_2)_2S + S$$

With rubber, the product would then have the empirical formula $C_{10}H_{16}SCl_2$. The results obtained by Meyer and Mark are shown in table 6. If Weber had had this compound, he would not have obtained the compound $C_{10}H_{14}S_2$ (32.3 per cent S) by the treat-

ment of $(C_{10}H_{16}SCl)_x$ with alcoholic sodium hydroxide, as mentioned below, because the sulfur content of $C_{10}H_{14}S$ is only 19.3 per cent.   All the work so far done on this problem has, therefore, not yet settled it.

The sulfur chloride compound is a white, insoluble powder which slowly decomposes giving off hydrogen chloride.   As in the case of sulfur vulcanization, no one has been able to isolate any of the sulfur chloride addition product from rubber vulcanized with sulfur chloride or from rubber gels prepared with the same reagent.   Only small amounts of the reagent are taken up during the ordinary vulcanization, probably not over 1–2 per cent. Articles so vulcanized are sometimes treated with ammonia to remove any hydrochloric acid that is formed at the same time (in part from moisture and the reaction with the non-rubber constituents).

When the rubber sulfur chloride product, $(C_5H_8SCl)_x$, is heated with an alcoholic solution of sodium hydroxide, all of the chlorine is removed along with the equivalent amount of hydrogen, and Weber found that a brown powder remains with the formula $(C_5H_7S)_x$, confirmed by complete elemental analysis. Hinrichsen and Kindscher repeated this experiment with one of their products, apparently selecting only the one that approximated the "half" addition product, $(C_{10}H_{16}SCl)_x$.   Their product contained 20.87 and 20.75 per cent of sulfur, and the calculated value for $(C_{10}H_{15}S)_x$ is 19.2 per cent.   The products are insoluble, inert and generally similar to hard rubber dust.

Weber (156) also treated rubber in solution with pure sulfur monobromide and obtained a product which lost hydrogen bromide readily, even during the purification.   Its sulfur content was higher and the bromine content lower than the values calculated for $(C_5H_8SBr)_x$.   However, upon being heated with aniline, it gave what was apparently the same compound as that obtained from sulfur chloride,—namely, $(C_5H_7S)_x$—and this was also confirmed by elemental analysis.   He concluded, therefore, that sulfur bromide adds like sulfur chloride.   The use of sulfur bromide as a vulcanizer is umpromising because of the loss of hydrogen bromide.   Gels can be formed with the reagent.   Sulfur mono-

iodide acts very slowly and the product is low in iodine. Removal of the iodine as hydrogen iodide with aniline gave a substance with only about one-fifth the required amount of sulfur, indicating that the reaction was very incomplete.

Selenium also vulcanizes rubber, as shown by Boggs (157). It is generally necessary to use an accelerator, and the amount of selenium chemically combined is probably very small. Selenium melts at 217°C., and its solubility in rubber has been shown by Williams (158) to be less than 0.05 per cent at 80°C. Fused mixtures of sulfur and selenium have certain advantages, especially in extending the life of the rubber product (159).

According to Frick (160), selenium oxychloride, $SeOCl_2$, reacts with rubber forming insoluble, amorphous substances which contain approximately 25 per cent of selenium and also of chlorine. The ratios are close to those of selenium and chlorine in the reagent. They also contain about the same amount of oxygen, indicating that considerable oxidation has taken place, and yet the content of hydrogen is proportionately very high. The products were prepared from several different kinds of rubber and from sodium-isoprene-rubber, and no formulas have been assigned to them.

5. Oxygen, ozone and oxidizing agents

Oxygen when pure or as in the air attacks rubber, especially in the presence of light, and slowly changes it to resin-like substances. Purified rubber is attacked very readily, whereas a good quality of crude rubber withstands the action of oxygen for a long time because of the presence of the naturally-occurring "antioxidant" discussed in the section on latex (p. 59). The action of oxygen has been studied on rubber films and on rubber in solution, and in both cases a number of products have been isolated and analyzed, and formulas such as $C_{25}H_{40}O_2$, $C_{10}H_{16}O_3$, and $C_{10}H_{16}O$ assigned to them (161) (162) (163). However, since the analytical results reported are not so close to those required by the theory as is desirable and since in the investigations only single experiments seem to have been carried out in many cases, these formulas have not yet been completely substantiated. They indicate that

oxygen adds progressively just as sulfur does. It has been demonstrated that peroxides are formed during the reaction and that therefore the reaction is probably one of autoxidation (164). In "tacky" rubber formed by exposure to air and light, Whitby (165) found levulinic aldehyde which was identified by the preparation of its pyridazine derivative. It is interesting to note that when air is passed into a benzene solution of rubber, the viscosity of the solution drops considerably. Similar changes have probably often been misinterpreted, especially when solutions have been heated in the presence of air, because the changes have been ascribed to depolymerization of the rubber complex, whereas they seem to be almost, if not entirely, due to oxidation. If air is kept out, the change in viscosity by heating is reversible (p. 70). Air oxidation to produce tacky rubber is accelerated in the presence of compounds of copper (166), manganese (167), iron (25), etc. Therefore these substances are rigidly excluded in the preparation of crude rubber and of rubber goods.

Excellent results have been obtained in this field by Pummerer and Burkhard (55), who found that the amount of oxygen gas absorbed by the pure rubber hydrocarbon in very dilute solutions at room temperature agrees very well with the formula $(C_5H_8O)_x$. The result was the same with or without platinum black, and the absorption was complete in 40 to 50 hours. The products were not isolated. The same authors also found that perbenzoic acid, $C_6H_5CO \cdot OOH$, reacted normally toward the rubber hydrocarbon, one mol being used for each C_5H_8 nucleus. The course of this reaction was followed by titration of the reagent and was verified by the isolation of the rubber oxide formed. It is a white, tough substance, much less elastic than rubber, and insoluble in all the ordinary solvents. The analysis is in excellent agreement with the formula $(C_5H_8O)_x$. Since previous work had indicated that the lowest compound with oxygen had the formula $(C_{10}H_{16}O)_x$, this newer work helps much to substantiate the C_5H_8 group as the fundamental group in rubber.

The action of ozone on rubber has already been discussed (p. 76). Mention should also be made of the fact that, according to Harries (168), when a solution of purified rubber is treated

with oxygen containing a high percentage of ozone which has not been passed through aqueous sodium hydroxide and concentrated sulfuric acid, there is formed an "oxozonide," $(C_5H_8O_4)_x$. This oxozonide resembles the normal ozonide in its properties although, strangely enough, in spite of its greater proportion of oxygen, it is not so explosive. On hydrolysis it gives the same decomposition products as the normal ozonide but in different quantities.

The rubber hydrocarbon is fairly stable toward potassium permanganate, and the use of this reagent in Baeyer's simple test for the double bond is not practicable. Harries (169), in his early work on rubber, tried to break it down with this reagent (2.5 per cent), but his results showed that a considerable amount of "depolymerization" took place and otherwise only a small portion was attacked, there being obtained "a small amount of fatty acids." Rubber that had been heavily milled or masticated was found to be more easily attacked than the unmasticated rubber, and yet no definite products were isolated. Boswell (163) has shown that a 7.5 per cent solution of permanganate acting on a 4 per cent carbon tetrachloride solution of rubber for five days, gives upon precipitation with methyl alcohol a white plastic mass which has the approximate empirical formula $C_{25}H_{40}O$. More recently, the action of permanganate has been studied in considerable detail by Robertson and Mair (170). These investigators used neutral and alkaline permanganate solutions of several different concentrations and isolated various acidic and neutral products. The acids consisted of formic, acetic, oxalic, levulinic and some complex colloidal resin acids. The neutral products contained increasing amounts of oxygen, more or less in proportion to the strength of the reagent used, and gave analytical results corresponding to such formulas as $C_{35}H_{56}O_4$, $C_{26}H_{42}O_6$, $C_{24}H_{38}O_6$, $C_{36}H_{56}O_5$, $C_{30}H_{48}O_{10}$, etc., which indicate approximate ratios of oxygen to C_5H_8 of from 1:9 to 5:3. They are insoluble in ethyl alcohol and acetone, and vary from pale yellow, slightly elastic substances to white, brittle substances. Nothing really very definite can be gleaned from this work beyond the fact that oxidation products containing varying amounts of oxygen can be obtained and that they are of high molecular weight, but it is

recorded here in order to emphasize the difficulties involved in the study of such a complex material as rubber.

These same authors also oxidized rubber with hydrogen peroxide and isolated as a primary oxidation product a mixture of a white pasty material of neutral reaction, with alcoholic properties and of the average composition $C_{59}H_{102}O_{16}$. This, along with the work just referred to, indicates that the size of the simplest rubber particle is not less than $C_{40}H_{64}$ or $(C_5H_8)_8$. Boswell, Hambleton, Parker and McLaughlin (163) give $C_{30}H_{48}O$ as the primary product of oxidation with hydrogen peroxide.

6. Hydrogen

Although the chemical reactions of the rubber hydrocarbon all indicated the presence of double bonds in its structure, until recently one of the chief reactions of such an unsaturated compound, hydrogenation, had not been realized. Harries (171) and Hinrichsen (172) had tried to hydrogenate it in the presence of platinum black, but without success. Doubt was, in fact, cast upon there being an unsaturated linking, and one author (163) a short time ago, after having failed in a similar attempt, placed himself on record against this hypothesis. He stated: "It is conceivable that the rubber molecule itself contains no double bonds whatever, and that these are only produced by the breaking up of the complex rubber molecule by the action of bromine or hydrochloric acid." The printing of his article was scarcely begun before a report of successful catalytic hydrogenation was being read at Leipzig by Pummerer and Burkhard (55) and an account of a similar and independent successful attempt was being published by Staudinger and Fritschi (103).

Pummerer and Burkhard found it necessary to use a solution with a concentration of less than 1 per cent and a rubber that was highly purified. In fact, in a later paper Pummerer and Koch (56) say that "a good criterion of the purity of the rubber is its behavior toward cold hydrogenation, since this reaction is very sensitive to impurities." A record of fifteen experiments is given in their first article demonstrating that at the ordinary temperature in the presence of a catalyst the rubber hydrocarbon adds two

atoms of hydrogen for each C_5H_8 nucleus.   The purified rubber was dissolved in either hexane or hexahydrotoluene, and a concentration of 0.2 to 0.6 per cent was found to be the best to obtain a complete reaction.   The catalyst was platinum black activated by oxygen according to the method of Willstätter and Waldschmidt-Leitz (173).   The total time necessary for the complete absorption of the gas varied from 3 to 170 hours, the shorter time usually at temperatures of 70–80°C.   By very careful work the hydrorubber was isolated and analyzed, and the results were found to check completely the theory for $(C_5H_{10})_x$. The hydrorubber, as isolated in the earlier experiments, was elastic, but later preparations were not.   This property probably depends on the treatment given the original rubber.   The hydrorubber of Pummerer and Burkhard is almost colorless and is soluble in ether, giving a colloidal solution.   The earlier preparations were very susceptible to air oxidation, especially in solution, but this property was later shown to be due to the presence of traces of the platinum black.   Pummerer and Koch repeated the earlier work, using purified rubber that gave a clear solution in ether and excluding air throughout the entire process.   The platinum black was not activated by oxygen, and on this account it was necessary to use a much larger amount, approximately ten times the weight of the sample.   A pressure of 0.5 atmosphere of hydrogen was used and the amount absorbed by the mixtures was much more than the theoretical, possibly on account of the larger amount of colloidal platinum.   These preparations of hydrorubber were stable toward air oxidation, and also stable toward bromine and potassium permanganate.   When dissolved in camphor the hydrorubber gave no depression of the melting-point, although when it was previously heated for twelve hours at 200°C. and then for twenty minutes at 300°C. under a pressure of 12 mm. of carbon dioxide, during which time no trace of decomposition was observed, it showed a molecular weight of 1700.

On distillation of the hydrorubber under 1 mm. pressure of hydrogen, no change occurred under 350°C., and the chief product (60 per cent of the original) appeared to be a saturated compound, $C_{50}H_{100}$ or $C_{50}H_{102}$; molecular weight (in camphor),

calculated, 700 or 702; found, 714. Its ether solution showed a distinct Tyndall effect. The difference between the molecular weight of the distilled product, 714, and that of the portion remaining in the distilling flask, 1500, together with that of the heated sample mentioned above, 1700, is discussed by the authors, and they consider that even saturated hydrocarbons may have residual valences and can be "aggregated" into higher "structures" ("Gebilden"), as is indicated by Gomberg's (174) addition products of hexaphenylethane and paraffins.

Staudinger and Fritschi's (103) method of hydrogenating rubber consists in the use of a catalyst but no solvent, and of very high temperatures and pressures. They employed ordinary platinum black which was incorporated into purified rubber by mixing it in a benzene solution, then precipitating it with alcohol and drying *in vacuo*. This platinized rubber without any solvent was placed in a glass container in a rotating autoclave filled with hydrogen at 93 atmospheres and heated for 10 hours at 270°C., or at 102 atmospheres and 280°C. Lower temperatures gave only partial hydrogenation. At ordinary pressure, but with the same high temperature, only partial hydrogenation was effected after 7 days with hydrogen passing through all the time. Nickel works much like platinum, but not so rapidly and completely. Their hydrorubber is a colorless, transparent, tough mass, without the elastic properties of rubber. The loss in color is said to be very characteristic of the reaction. The analyses check very closely the empirical formula, $(C_5H_{10})_x$, and the authors state that according to the properties of the hydrorubber it can be considered as a saturated hydrocarbon with so great a molecular weight that, so far as can be shown by analysis, no distinction can be made between $C_{5x}H_{10x}$ and $C_{5x}H_{10x+2}$. The product is soluble in benzene, chloroform and ether, and insoluble in alcohol and acetone. Its solutions are colloidal, and in benzene it shows no depression of the freezing-point. Its solutions do not decolorize bromine solution, but on standing in the sunlight a substitution product is formed with the evolution of hydrogen bromide. By complete bromination, followed by removal of the bromine as hydrogen bromide, a regenerated rubber is obtained. The hydro-

rubber is unattacked by sulfur monochloride in solution, being recovered unchanged, whereas rubber itself is vulcanized by this reagent.

Harries (175) criticized the work of Staudinger and Fritschi, saying that their hydrorubber might be hydrogenated pyrogenetic decomposition products of rubber. But Staudinger (176), in reply, pointed out (1) that such products would not be colloidal because they are of finite molecular weights; (2) that the hydrorubber has the properties of a paraffin hydrocarbon, and is, in fact, the first known colloidal paraffin; and (3) that the lowest-boiling heat-decomposition product of their hydrorubber was proved to be methylethylethylene,

$$CH_3 \cdot CH_2 \cdot \underset{\underset{\displaystyle CH_3}{|}}{C} =\!\!=CH_2$$
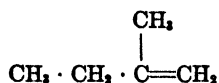
Therefore, the hydrogenation of the rubber must have taken place before any decomposition of the rubber had set in. He also repeated Pummerer and Burkhard's work, but used a temperature of 100°C. and 60 atmospheres pressure. The product was apparently the same as that obtained without the use of a solvent, and was much tougher than the high temperature product.

Dry distillation of the high-temperature hydrorubber (103) at 350–400°C., under 1 mm. pressure, gave a series of olefins and only a small residue (0.6 per cent). As already mentioned, the lowest member was found to be methylethylethylene, C_5H_{10}. The amount was about 5 per cent. From the remainder of the distillate there was isolated $C_{10}H_{20}$, $C_{15}H_{30}$, a mixture of $C_{40}H_{80}$ and $C_{45}H_{90}$, and $C_{50}H_{100}$ which boiled at 268–75°C. at 0.014 mm. and was equivalent to 24 per cent of the crude distillate. The isolation of these olefins shows that there is no doubt that the hydrogen is combined with the double bonds of the rubber-hydrocarbon just as it can be combined with any ordinary olefins.

Harries (177), after his work on shellac in which he was able to change the alcohol-insoluble, "aggregated," unreactive form into the alcohol-soluble, "disaggregated," reactive form, believed that rubber had not been hydrogenated because it was in the aggre-

gated, unreactive form. He, therefore, tried to hydrogenate rubber which had been thoroughly plasticized or masticated on the mill, and was successful. He used platinum black as his catalyst, and applied for a patent in April, 1921 (178), seventeen months before the first publications discussed above. He, evidently recalling his bitter experience in his fight for priority in the synthesis of rubber, remarks "but I expressly state that I do not wish to use this fact as the basis for any claim of scientific priority over Pummerer." He published no analytical results on his hydrogenated rubber.

It should be added that Pummerer and Koch (56), in the course of their study of hydrogenation, also found that when no excess of pressure was used and the time was therefore much longer than usual, they sometimes obtained products which were stable toward bromine, that is, chemically saturated, and yet were low (about 1.5 per cent) in hydrogen according to the analyses. They therefore concluded that since the substance shows the presence of no double bonds when treated with bromine, the double bonds must have entered into reaction with one another, presumably by internal ring formation.

As already mentioned, high temperatures cause more or less internal ring formation (polycyclization) and Staudinger (71) and his co-workers found that at the high temperatures used by them for the hydrogenation of rubber, considerable polycyclorubber was formed along with the hydrorubber unless a rapid reaction with an active catalyst was obtained. The polycyclorubber absorbs much less hydrogen under similar conditions. The hydro-polycyclo-rubber does not add bromine and is not attacked by hot nitric acid and cold potassium permanganate, whereas the polycyclo-rubber itself reacts with all these reagents.

Staudinger (179) has made the interesting observation that the hydrogenated hydrocarbons of rubber, gutta-percha and balata are, according to the analyses and refractive indices, identical.

$$n_D^{16}$$

Hydrorubber....... .... 1.4768
Hydrogutta-percha... 1.4740
Hydrobalata.. .... 1.4762

7. The "nitrosites"

Terpenes add nitrogen trioxide, N_2O_3, forming nitrosites. For example, α-terpinene forms the nitrosite, $C_{10}H_{16}N_2O_3$. It was known for many years that gases containing certain oxides of nitrogen harden rubber tubing and rubber stoppers, and these facts led Harries to study the action of nitrogen trioxide on purified rubber. The compounds formed (180) are yellowish powders which are usually soluble in acetone, ethyl acetate and aqueous alkalies, and insoluble in benzene and ether. They slowly decompose with loss of nitrogen or its oxides. At 80°C. this decomposition is more noticeable, and at higher temperatures it is quite rapid. On this account it is very difficult to analyze the compounds. Furthermore, the purity of the gaseous reagent, the oxidation due to prolonged action, and the slow decomposition even during purification, together with the difficulties of analysis, have all tended to cause considerable difficulty and some controversy in the interpretation of the results. The work on these substances is well summed up in Harries's book referred to above, and in Rosenbaum's translation of Gottlob's "Technology of Rubber." The chief product appears to be Harries's "nitrosite C," for which he obtained excellent analytical results and a molecular weight determination by the Landsberger-Rüber method in acetone corresponding to $(C_{10}H_{15}N_3O_7)_2$. A true nitrosite of similar molecular weight would have the formula $(C_{10}H_{16}N_2O_3)_2$. "Nitrosite C" decomposes at 158–62°C. Oxidation with potassium permanganate gives a mixture of aliphatic acids consisting chiefly of succinic and oxalic acids. The formation of "nitrosite C" was adapted by Harries (181) to the quantitative determination of the rubber hydrocarbon in crude and in vulcanized rubbers. After the nitrosite is formed it is isolated and weighed as such, or its carbon may be determined by combustion (182).

Weber (183) studied the action of nitrogen tetroxide, N_2O_4, on rubber in solution and claimed to have isolated a substance with the formula $(C_{10}H_{16}N_2O_4)_x$. Several other investigators have tried but have been unable to obtain this "nitrosate." Weber reported but a single analysis which agreed very well with the

theory, but all others have found much more oxygen than is accounted for in his formula. Harries (184) states that the product closely resembles his "nitrosite C." Very recently Emden (185) has carefully reinvestigated the whole question. He used purified rubber and worked at temperatures around 0°C., where the N_2O_4 is practically not at all dissociated into NO_2. The N_2O_4 and rubber were separately dissolved in carbon tetrachloride and the solutions mixed, with the N_2O_4 always kept in excess. The time interval was short and never over 2 hours. The product in each case is pure white, sinters at 90–5°C. with incipient decomposition, reduces hot Fehling's solution, and does not dissolve in dilute ammonium hydroxide even after several days, but does dissolve gradually in aqueous sodium hydroxide. It dissolves only slowly in acetone, finally giving a clear red-brown solution from which it can be reprecipitated with water. This precipitate is slightly yellow and is now easily soluble in acetone. The original compound dissolves readily in hot acetone and no gases are evolved during the heating. The products from plantation rubber and guayule are apparently the same. The yields and the analyses agree with the composition $C_{10}H_{16}N_2O_6$. No molecular weights are recorded. The author thinks that the compound $C_{10}H_{16}N_2O_4$ is probably not capable of existence, that the addition of N_2O_4 is accompanied by oxidation and that the nitrosate $C_{10}H_{16}N_2O_6$ may be regarded as the primary product of the reaction. When rubber and an excess of N_2O_4 are allowed to stand for 24 hours at room temperature, the product becomes easily soluble in acetone, dilute ammonium hydroxide and sodium hydroxide, and when refluxed in acetone now evolves 0.1 mol of carbon dioxide. No analyses are given for these products. The author believes that the formation of this nitrosate can be satisfactorily used in a method of analysis.

8. Nitrones

In 1915 Allesandri (186) found that nitrosobenzene formed an addition product with the rubber hydrocarbon and gave it the following approximate composition, $C_{58}H_{61}O_9N_5$. Bruni and Geiger (187) studied this reaction in greater detail and prepared

some very interesting derivatives. Angeli, with whom Allesandri had worked, discovered and explained the action of nitrosobenzene on olefinic compounds in 1910. He showed that two mols of nitrosobenzene react with the double bond, one adding and the other oxidizing, the latter being reduced to phenyl hydroxylamine which in turn reacts with a third mol of nitrosobenzene forming azoxybenzene:

$$R \cdot CH_2 \cdot CH : CH_2 + 2\ C_6H_5NO \rightarrow R \cdot CH : CH \cdot \overset{H}{\underset{}{C}} : \overset{O}{\underset{}{N}} \cdot C_6H_5 + C_6H_5NHOH$$

$$C_6H_5NHOH + C_6H_5NO \rightarrow C_6H_5 \cdot N : \overset{O}{\underset{}{N}} \cdot C_6H_5 + H_2O$$
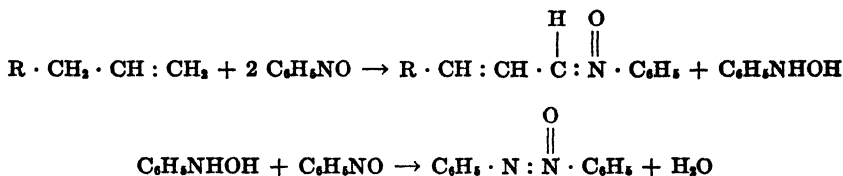
It should be noted that the position of the double bond has shifted. The reaction between nitrosobenzene and rubber takes place readily when they are mixed in benzene solution in the proportion of 3 mols to each C_5H_8 group, and warmed for a few minutes on the steam bath. The product is precipitated by means of petroleum ether. It is a powder, has the empirical formula $C_{11}H_{11}ON$, and decomposes at 135–40°C. From the mother liquor, azoxybenzene can be obtained. The product contains a double bond as shown by the addition of bromine, giving $C_{11}H_{11}ONBr_2$. These facts all prove that the reaction is similar to that outlined above. It can be formulated as follows:

$$\left[\begin{array}{c} CH_3 \\ | \\ -CH_2 \cdot C : CH \cdot CH_2- \end{array} \right]_x + 2x\ C_6H_5NO \qquad \begin{array}{c} CH_3 \\ | \\ -CH : C-C-CH_2- \\ \quad \overset{||}{N}=O \\ \\ C_6H_5 \end{array} \quad \text{or}$$

$$\begin{array}{c} CH_2 \\ || \\ -CH_2-C-C-CH_2- \\ \quad\ \overset{||}{N}=O \\ \quad\ | \\ \quad\ C_6H_5 \end{array} \ + x\ C_6H_5NHOH$$

$$C_6H_5NHOH + C_6H_5NO \rightarrow C_6H_5N{=}\overset{O}{N} \cdot C_6H_5 + H_2O$$
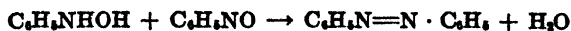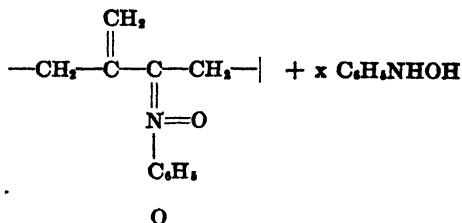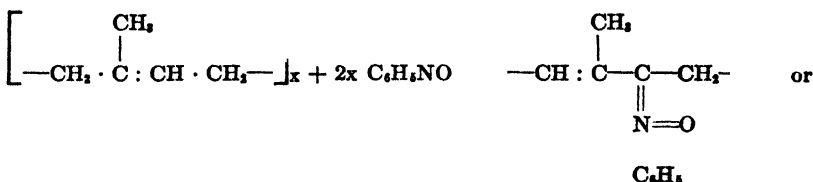
The position of the double bond in the new derivative has not yet been established, but it is probably in the first of the two places indicated. Since the position of the double bond is different from that in the natural rubber hydrocarbon, the new product is a derivative of an isorubber, and has been termed a nitrone of isorubber. The same reaction occurs when latex of *Hevea brasiliensis* is diluted with pyridine and mixed with nitrosobenzene in pyridine.

Solutions of the nitrone show colloidal properties, and when examined by x-rays, the photographs give no indication of even minute crystals. The reaction is rapid and complete, and the authors expect to be able to adapt it to a quantitative method of determining the rubber hydrocarbon.

Phenyl hydrazine reacts with the nitrone and a phenyl hydrazone of isorubber is thus formed:

$$\begin{array}{c} CH_3 \\ | \\ -CH\!=\!C-C-CH_2- \quad + \ x \ C_6H_5NHNH_2 \\ \| \\ N\!=\!O \\ | \\ C_6H_5 \end{array}$$

$$\begin{array}{c} CH_3 \\ | \\ -CH:C-C-CH_2- \quad + \ x \ C_6H_5NHOH \\ \| \\ NNHC_6H_5 \end{array}$$
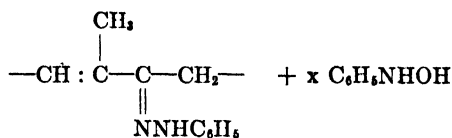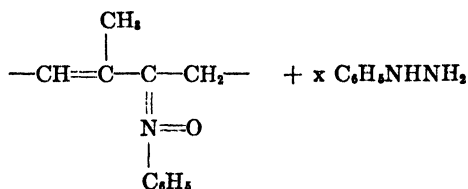
It is expected that this hydrazone can be hydrolyzed and a ketone of isorubber prepared.

True nitroso compounds react with rubber like nitrosobenzene itself. *o-*, *m-*, and *p-*Nitrosotoluene and the methyl ether of *o-*nitrosophenol, *o-*nitrosoanisole, form the corresponding nitrones. Ethyl *o-*nitrosobenzoate reacts similarly. On hydrolysis it gives the free acid which is insoluble in water, but the potassium salt is readily soluble. The solution has the character of a true salt solution and the authors point out that here is a typical

case of a colloidal electrolyte with a colloidal anion and molecularly dispersed cations.

$$\left[\begin{array}{c} O \\ \| \\ -C_5H_6 : N \cdot C_6H_4 \cdot COOK \end{array}\right]_x \rightleftharpoons \left[\begin{array}{c} O \\ \| \\ -C_5H_6 : N \cdot C_6H_4 COO^- \end{array}\right]_x + x\ [K^+]$$
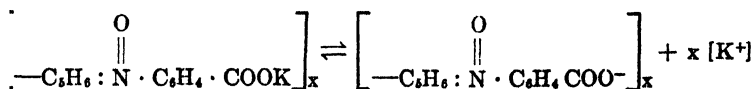
The hydrocarbon of gutta-percha gives a nitrone similar to that of rubber.

Further work is promised and should yield important results. It should be mentioned that the work of Bruni and Geiger is only a report and contains no analytical data.

Pummerer, Andriessen and Gündel (188) have substantiated the above work and have found it necessary to prepare the isorubber nitrone in the absence of oxygen. The molecular weight in benzene and in nitrobenzene is 1200–1400, corresponding to eight isoprene groups. The calculated value for $(C_{11}H_{11}ON)_8$ is 1384.

9. Tetranitromethane

Tetranitromethane unites with olefin hydrocarbons to give yellow unstable addition products (189), and Pummerer and Koch (56) found the reaction useful in proving the completeness of the hydrogenation of rubber. Pummerer and Pahl (20) have now shown that in hexahydrotoluene solution the reaction mixture at first turns yellow, and after 5 to 6 days (at 0°C.) it becomes almost colorless or only faintly yellow or pink, and a stable addition product separates. It does not lose tetranitromethane even when dried in a high vacuum for 6 hours at 60°C. The reagent is therefore probably bound by primary valences to the rubber. Upon analysis it is found that not all the double bonds react, since under the conditions used one mol of tetranitromethane corresponds to 4.5–6 C_5H_8 groups. There is no oxidation, because the ratio of nitrogen to oxygen remained as in the reagent, namely 1:2. With pale crêpe or smoked sheet, pure rubber or gel-rubber in suspension or completely broken down on the mill, the ratio of rubber to the reagent is 1:5, but with sol-rubber or with the completely broken down purified rubber obtained by the alkaline

treatment of latex, it is 1:6.   In higher concentrations of pure
rubber the ratio is sometimes 1:4.   The differences may be due
chiefly to colloidal factors not fully understood.

The rubber tetranitromethanate suspended in inert solvents
still decolorizes bromine.   No data, however, are given to show
whether an addition product is formed or whether the bromine
simply replaces the tetranitromethane.   From the present ac-
cepted structure of tetranitromethane the partial structure of the
product may be indicated as follows:

$$O : N—\dot{O} \quad \dot{C}(NO_2)_3$$
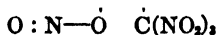
10. Nitric acid

Concentrated nitric acid reacts slowly with crude rubber in the
cold, but on warming or adding fuming nitric acid the reaction
may become very violent.   In any case a solution is finally
obtained which when poured into water gives a voluminous, yel-
low, flocculent precipitate.   The yield of the dry yellow powder is
surprisingly constant, about 22 per cent.   This nitric acid prod-
uct is soluble in ethyl acetate, acetone, benzaldehyde, nitro-
benzene, aniline, acetic anhydride and aqueous alkalies with a
deep maroon color.   Although the reaction is one that was
known for a long time, Ditmar (190) seems to have been the first
one to study the product and analyze it.   He found that it could
be methylated and acetylated and that it could be reduced with
sodium methoxide.   Since the substance was somewhat explosive,
its combustion analysis was difficult.   The results varied as
much as 2 per cent in the carbon, but the averages and the molec-
ular weight determination approximated the formula $C_{10}H_{12}N_2O_6$.
On the basis of this formula and of results obtained by ti-
tration with alkali and on the assumption that rubber was
related to dipentene, he suggested that the compound was
"5,6-dinitro-2,5-dihydrocumic acid."   This formula, given twenty-
eight years ago, has never been verified.   From our present
knowledge nothing definite structurally is known of this product.
Harries (191) repeated Ditmar's work and stated that in general

he substantiated Ditmar's results, although he gave no analytical figures. He found that on concentration of the aqueous filtrate considerable oxalic acid crystallized out and the residual liquor contained a very soluble, syrupy, nitrogenous acid whose silver salt had the approximate composition $C_6H_8NO_5Ag$. The writer might add that recalculation of Harries's results shows that the acid might be a nitrolevulinic acid, $C_5H_7O_5N$. This structure would be logical but it has not yet been substantiated. The same or a similar nitric acid product of rubber can be obtained by the prolonged action of dilute nitric acid on thin strips of rubber (192).

A different product has been obtained by Fisher (193) from nitric acid and rubber. He uses a carbon tetrachloride solution of rubber. The yield from a 5 per cent solution and an excess of concentrated nitric acid is approximately quantitative for a substance having the formula $(C_5H_7NO_2)_x$. Like Ditmar's nitric acid product it is unstable toward heat and is difficult to analyze. The highest nitrogen determination checked the theoretical value for the formula given, but a good duplicate determination has not yet been obtained. The substance is a bright yellow, slightly hygroscopic powder which is soluble in the same solvents as those mentioned above, but insoluble in sodium carbonate solution, whereas Ditmar's product is soluble in sodium carbonate solution. The new product decomposes slowly at room temperature and explodes when heated. It can be alkylated and acylated, forming compounds which are much more stable toward heat. Its unsaturation as determined by the iodine chloride method in a 1 per cent nitrobenzene solution was found to be 24.8 per cent of the unsaturation calculated for a nitro-rubber. It is very probable that the nitric acid has caused the change in unsaturation just as other acids do, and the product is therefore probably a nitro-poly-cyclo-rubber.

11. Chromyl chloride

The terpenes react readily with chromyl chloride forming addition products, $C_{10}H_{16} \cdot 2CrO_2Cl_2$, which are decomposed by water into aldehydes or ketones, chromic acid, etc. Spence and

Galletly (194), in 1911, found that chromyl chloride also reacts with rubber forming a similar addition product, to which they gave the same formula $C_{10}H_{16} \cdot 2CrO_2Cl_2$. Since very complex substances are obtained from it, and the molecular weight has not been determined, the formula should probably be written $(C_5H_8 \cdot CrO_2Cl_2)_x$. Robertson and Mair (170) have recently confirmed the formation and composition of this product. The substance is a brownish powder, insoluble in nearly all organic solvents. It is soluble in alcohol and acetone with decomposition, and in water by which it is immediately decomposed into resinous products. The decomposition products can be separated by alcohol and acetone into a soluble portion which has the properties of an aldehyde, and an insoluble portion which is of indefinite composition and contains chromium and chlorine. The aldehydic substance was converted into a phenylhydrazone by the first investigators and into a semicarbazone by the second. Oxidation transforms it into a resin acid and a complex insoluble product. Spence and Galletly found that what appeared by analysis to be the same chromyl chloride addition product was obtained from rubber of very different sources. They tried to use the reaction in a quantitative way but could not very well because of the rapid decomposition of the product by moisture.

12. Stannic chloride, ferric chloride, etc.

Stannic chloride reacts with the rubber hydrocarbon in benzene solution to form colored addition products, as recently shown by Bruson, Sebrell, and Calvert (195). The two products formed remain in solution and are isolated by evaporation of the liquid *in vacuo* at 70°C. The residue forms a reddish-brown, brittle vitreous solid, which redissolves with difficulty in benzene. In moist air it slowly decomposes, evolving fumes of stannic chloride. It slowly decomposes when heated, and at 170°C. swells and evolves copious fumes of stannic chloride. All the operations must be carried out in a dry inert atmosphere because the products are very hygroscopic and readily oxidize in the air.

Complete elemental analyses agree very well with the empirical composition $(C_5H_8)_{10} \cdot SnCl_4$. The substance dissolves in alcohol,

but at the same time the stannic chloride is split off, remaining in solution, and the hydrocarbon is simultaneously precipitated as a white amorphous powder. This powder has the same composition as the original rubber hydrocarbon, $(C_5H_8)_x$, but is less unsaturated. Therefore, it no doubt belongs to the polycyclic rubbers already mentioned and discussed below. The authors call it a "polymeride." Maybe it is. Definitions in rubber chemistry are at present in a state of flux. The amorphous powder consists of two substances of the same composition, and of the approximate ratio 3:1, as shown by their solubility in benzene, the greater proportion being the soluble variety. It is from this difference that it is inferred that there are two addition products formed, as stated at the beginning. The authors show satisfactorily that the soluble and insoluble "polymerides" come from the corresponding varieties of rubber—the sol- and gel-rubbers—and offer these facts as additional evidence for the "two-phase" system of rubber.

The authors assume the validity of Staudinger's chain theory of the structure of rubber with free end valences (196), and conclude that the addition of the stannic chloride occurs at these end valences. "Since $SnCl_4$ possesses two reactive secondary valences, it is probable that two molecules of rubber hydrocarbon add to the $SnCl_4$ in such a manner that upon subsequent treatment with alcohol some of the double bonds of the hydrocarbon bridge across to form rings in the more reactive positions of the double molecule, leaving other unsaturated bonds intact." This is a graphic explanation but is supported by no experimental demonstration. The authors have, however, shown very nicely that 1 $SnCl_4$ reacts with 10 C_5H_8 groups, thus giving added evidence as to the size of the reactive portions of the rubber molecule.

Titanium tetrachloride behaves like stannic chloride, giving both the soluble and insoluble "polymers" of rubber. Ferric chloride and antimony pentachloride react to give insoluble jellies, which with alcohol form white insoluble "polymerides" of rubber even when sol-rubber is used. These three reagents must be used in chloroform or carbon tetrachloride solutions because they react with benzene.

13. Sulfuric acid

Everyone working in a laboratory is familiar with the fact that concentrated sulfuric acid reacts with rubber tubing and stoppers. It also reacts slowly with crude rubber, as has been known for many years. It finally dissolves the rubber, slowly oxidizing it at the same time. Kirchhof (197) has isolated from such a solution an aldehydic acid to which he has given the formula $C_{20}H_{30}O_3$.

Harries (198), in an effort to polymerize rubber into a higher modification and perhaps convert it into gutta-percha, tried the action of concentrated sulfuric acid on a benzene solution of rubber. It was rapidly transformed into an insoluble variety which separated as flocks. This amorphous precipitate was washed with aqueous sodium carbonate but could not be freed from ash. Harries believed, however, that the powdery product had the same composition as the rubber hydrocarbon, but that it was of a higher molecular weight.

Marquis and Heim (199) used this same reaction in chloroform solution as a quantitative method for estimating the rubber hydrocarbon. When the amount of acid was not too great and the time of shaking not too long, they obtained a white, amorphous powder which was soluble in chloroform and benzene, and contained no sulfur. The analysis of the product did not check up exactly for C_5H_8, and they thought that the acid had caused the addition of the elements of water. The discrepancy can probably be accounted for by oxidation. Increase in the amount of acid or in the time of the reaction gave an insoluble product.

During the last few years Kirchhof (197) has continued this work, has substantiated the foregoing, and has shown from the bromine content of the reaction product with bromine that the "sulfuric acid-rubbers" are probably not more than about one-quarter as unsaturated as rubber. Since bromine substitutes as well as adds in these cases, the unsaturation may even be a little less because the analytical value represents the maximum. Samples which are heated with sulfur contain not over 10 per cent of combined sulfur, which is equivalent to approximately 25 per cent of the unsaturation of rubber. Ozonization work gives

no levulinic aldehyde, because no products are formed that give the pyrrole reaction. Concentrated sulfuric acid also produces similar products directly from latex. It is almost impossible to obtain these products pure, and they generally contain a small amount of ash and sulfur. Kirchhof stated that the decrease in unsaturation was probably due to the mutual saturation of some of the double bonds in the rubber molecule, forming tetramethylene rings, but later added that it might be due to some other form of cyclization. The softer varieties of wild rubbers give products which soften under moderate heat and can be molded. When melted they are converted into hard shellac-like substances which are soluble in benzene.

Fisher (200) found that concentrated sulfuric acid can be mixed directly into rubber on a rubber mill, and when batches containing 5 per cent of the acid are heated under various conditions they are converted into moldable thermoplastic masses. The products are somewhat oxidized, are only partially soluble in benzene and chloroform, and are much less unsaturated than rubber itself.

If one part of rubber dissolved in petroleum ether is treated with ten times its weight of concentrated sulfuric acid, and then with three times its weight of formalin, two parts of an insoluble powder is obtained. Kirchhof (201) has named this "rubber formo-lite." Heating does not melt but simply chars it. Bromine reacts with it, probably adding and substituting, the resulting product containing only 12.6 per cent of bromine.

14. Polycyclo-rubbers

In the last section an account was given of Harries's (198) attempt in 1910 to polymerize rubber into gutta-percha by treating it in solution with sulfuric acid. Although he was unable to free the resulting powdery, non-elastic product from inorganic salts, he considered that it had the same empirical formula as rubber but that it was in a higher state of polymerization.

Ostromislenski (202), by comparing the properties of polyvinyl bromide and erythrene-rubber dibromide, found that when the latter was heated with zinc dust the bromine was removed and a hydrocarbon formed, to which he assigned the formula

$C_{32}H_{48}$ and for which he coined the name "cauprene" (from kaut-schuk and polyprene). Cauprene adds much less bromine and hydrogen chloride than would be expected, forming compounds with the formulas $C_{32}H_{48}Br_4$ and $C_{32}H_{48} \cdot 2HCl$, respectively. These are saturated compounds and he therefore concluded: "the formation of cauprene from cauprene bromide, its composition, the composition and chemical character of the bromide and hydrochloride of cauprene, characterize it as a representative of a new, peculiar class of 32-membered polycyclic hydrocarbons."

Kirchhof (197), as also described in the previous section, studied further the action of sulfuric acid on rubber in solution and found that the products were about 25 per cent as unsaturated as the rubber hydrocarbon itself. He concluded that sulfuric acid does not polymerize the rubber hydrocarbon but changes it into a new hydrocarbon, physically and chemically distinct, and probably containing tetramethylene rings.

At about this same time Harries and Evers (141), by the action of zinc dust on a solution of rubber hydrochloride containing an excess of free hydrogen chloride, obtained a hydrocarbon which was thermoplastic, and from a series of varying analyses concluded that they had prepared a partially hydrogenated rubber of the formula $(C_{10}H_{18})_4$, to which they gave the name "alpha-hydrorubber." Later, Staudinger and Widmer (85) in repeating the work of Harries and Evers, and using the hydrobromide as well as the hydrochloride, found that the product is not a hydrorubber, because it has the same empirical formula as the rubber hydrocarbon, and, from the absorption of bromine, that it is less than half as unsaturated as the rubber hydrocarbon. Harries and Evers had prepared the hydrochloride and the ozone derivative, and a study of the analytical figures for these substances also shows approximately the same change in the unsaturation. The product is therefore a cyclic rubber.

In the course of their work on the destructive distillation of rubber, Staudinger and Fritschi (203) reported that the resinous residue, according to its bromine absorption, was approximately one-half as unsaturated as the rubber hydrocarbon. Staudinger continued the study of the action of heat on rubber and with

Geiger (95) gave a complete account of this work (see p. 72). The change in unsaturation begins to take place around 200°C. and is rapid above 270°C. An almost quantitative yield of the product with the lesser unsaturation is obtained when rubber in the presence of ether is heated in an autoclave for two days at 250° C. The product can be isolated by precipitation with alcohol. Fisher and A. E. Gray (52) obtained similar products from rubber which had been heated in sealed tubes.

Fisher (200), working independently, discovered that by mixing comparatively small amounts, approximately 10 parts to 100 of rubber, of an organic sulfonyl chloride or an organic sulfonic acid into rubber on the mill, and then heating the mix in sheet form at 125-35°C., the rubber is converted into tough, thermoplastic products resembling gutta-percha and hard balata. If heated simlarly in bulk there is a pronounced exothermic reaction and the products formed are hard and thermoplastic, like shellac. A study of the chief constituents of these various products, wherever it was possible to isolate them, shows that they consist of hydrocarbons of high molecular weight with the same composition as that of rubber, $(C_5H_8)_x$ (204). In order to differentiate these products which are isomeric with rubber, they have been given the general name "thermoprene," signifying a thermoplastic unsaturated hydrocarbon derived from polyprene, Weber's name for the rubber hydrocarbon. In order to distinguish between the varieties, certain letters are added to signify the type, such as GP for gutta-percha, HB for hard balata, and SL for shellac-like, —for example, thermoprene-GP.

The addition products formed with rubber in solution by the action of stannic chloride, ferric chloride, etc. (p. 112), when treated with alcohol also give products of these same general characteristics. The action of aluminum chloride (205) is probably also fundamentally the same. Staudinger (85) concluded that the action of zinc dust and hydrogen chloride on the rubber hydrochloride in solution really consists of the action of zinc chloride on the rubber (or isorubber) regenerated from the hydrochloride by the loss of hydrogen chloride, because he found that zinc chloride converts rubber in solution into a less unsaturated hydrocarbon. The product, however, is soft and sticky.

When rubber is mixed on the mill with ferric chloride, ferric bromide, or other amphoteric metal halides, and the mixture heated at about 175°C., it is converted into similar products which probably are of the same type of less unsaturated rubber hydrocarbons (206).

Other methods of isomerizing rubber have also been developed by Fisher (207). These consist of heating rubber with such agents as trichloroacetic acid, concentrated hydrochloric acid, diphenylamine hydrochloride, pinene hydrochloride, etc., chiefly in the presence of phenols, sometimes in solution and sometimes not. Pummerer, Nielsen and Gündel (72) have cyclicized sol-rubber by heating it for several hours at 90°C. and 60 atmospheres of hydrogen in the presence of platinum black. When nitrogen was used there was no cyclization. A very interesting method of isomerizing rubber has been discovered by Fromandi (208). It consists of the action of a high tension alternating current on a solution of rubber in decalin in an atmosphere of hydrogen.

Although these substances vary considerably in their physical characteristics, from rubbery types through the gutta-percha and hard balata types to hard shellac-like types, all, when pure, consist of a hydrocarbon or a mixture of hydrocarbons with the formula $(C_5H_8)_x$ and have less unsaturation than that of the rubber hydrocarbon itself. The unsaturation varies from about 57 per cent of that of rubber to about 20 per cent. Since there is no change in the composition, and since the molecular weights are not definitely known, the only explanation at present is that the change in unsaturation must be due to internal cyclic formation.

Staudinger spoke of these products as monocyclo-rubbers and polycyclo-rubbers, depending upon whether the unsaturation was half or less than half that of rubber. They have also been spoken of as polymers of rubber. Polymerization of unsaturated hydrocarbons involves the loss of double bonds, and since the new products are less unsaturated than the starting material it would seem at first as if this were a proper designation. Polymerization would also involve an increase in the molecular weight. Now the soluble products form solutions which show typical colloidal properties, and molecular weight determinations give values

from 8500 to 1570, depending partly on the solvent employed (73). These figures compare favorably with those for rubber itself and indicate that there is no increase in the size of the molecular particle. The molecular weights of the insoluble products are not known. These may be very high.

If the products had the same molecular weight as that of the rubber from which they are prepared, then they would be called isomers and, more particularly, metamers. It is not certain whether they do have the same molecular weight, although this is indicated in some of the known results. Since there is no change in composition, the reaction is an isomerization and the products are therefore rubber isomers, if we use this term in its generic sense. It would seem best to use the term "rubber isomer" and not "isorubber," because this latter term should be kept for those derivatives which are more strictly isomeric, for example, position isomers, such as Harries's isorubbers obtained from the hydrochloride, and for the parent substance of Bruni's nitrones.

Other physical constants also substantiate the conclusions discussed above,—namely, that the products have an internal cyclic formation. Most of the examples given below are from the work of Staudinger and his collaborators.

The density is greater than that of rubber: for the rubber hydrocarbon d_4^{17} = 0.920; for polycyclo-rubber d_4^{17} = 0.992. The terpene hydrocarbons show similar increases in going from an open chain $C_{10}H_{16}$ compound to a monocyclic and to a bicyclic compound:

Myrcene = 0.803	Limonene = 0.845	Pinene = 0.862
(open chain)	(monocyclic)	(bicyclic)

The molecular refraction indicates the loss of double bonds and shows good agreement with the calculated values:

Rubber hydrocarbon n_D^{18} = 1.5222 Polycyclo-rubber n_D^{17} = 1.5387

$M_{D(100)}$ $(C_5H_8)_4 + 4$ ⌐ Calculated* 32.28 Found for rubber, 32.19.

$(C_5H_8)_4 + 1$ ⌐   "   31.36.   "   " polycyclo-rubber, 31.56.

* These calculations are based on an unsaturation of 25 per cent of that of the rubber hydrocarbon, that is, the loss of 3 out of every 4 double bonds. The symbol ⌐ stands for "double bond," and the molecular formula is given just for unit comparison.

The heat of combustion of polycyclo-rubber is less than that of rubber:

Polycyclo-rubber ....10,500 calories per gram
Rubber hydrocarbon........................ 10,970 calories per gram

Kirchhof's figure for sulfuric acid-cyclicized rubber is 10,075 calories, recalculated to ash-, sulfur- and oxygen-free sample, because his product could not be purified properly (209). Weber (210) gives 10,669 calories for the rubber hydrocarbon. The figure given in the comparison above was obtained by Messenger (211) and is the most accurate yet published. It follows therefore that the cyclization, as would be expected, is an exothermic reaction. This is in accord with the facts.

The products formed by cyclization are, when pure, white in powdered form, and amber-colored in the melted condition. The x-ray spectrograms show them to be amorphous substances. When soluble, they dissolve in benzene, chloroform, carbon tetrachloride, carbon bisulfide, gasoline, turpentine, tetralin, sometimes in ether, and do not dissolve in alcohol and acetone. These solutions vary in color from colorless to yellowish or yellow-green. They are much less viscous than solutions with corresponding amounts of ordinary masticated rubber. Concentrations of 25 per cent are easily obtained. The softening and melting points depend on the method of preparation, varying from room temperature to 280°C. They are much more stable toward heat than is rubber, as already mentioned. Extensive decomposition does not begin until about 350°C. The distillate contains neither isoprene nor dipentene but consists of other terpenes and polyterpenes. If any isoprene is formed it is completely polymerized by the heat.

The amount of unsaturation is determined by titration with bromine or iodine chloride solutions. Bromine substitutes rather vigorously sometimes. The results obtained have been checked in a few cases by other means,—for example, by analyzing the addition products formed with hydrogen and with sulfur. Sulfur under vulcanizing conditions adds chemically, converting the polycyclo-rubbers (thermoprenes) eventually into hard, insoluble

non-thermoplastics. This change resembles the formation of hard rubber. If the thermoprenes are saturated with sulfur in solution they remain soluble and thermoplastic. The highest amounts of sulfur found by heating direct mixtures and solutions are 21.11–21.78 per cent, corresponding to 57.5–59.0 per cent unsaturation (204). Sulfur chloride in a solution slowly forms a gel, and the isolated products show irregular amounts of sulfur and chlorine (204). Hydrogen chloride and hydrogen bromide add in various amounts, apparently because they cause a further change in the unsaturation during the reaction. Sulfur chloride probably does the same thing.

The polycyclo-rubbers slowly absorb oxygen from the air. Ozone forms an insoluble product which is quite different from rubber ozonide in that it is not explosive. Furthermore, when boiled with water it yields no levulinic aldehyde or acid. Analysis, in fact, shows that it is not an ozonide but a simple oxide $(C_5H_8O)_x$. This composition is the same as that of the rubber oxide obtained with perbenzoic acid from rubber. A similar product of the same composition has also been obtained from thermoprene-GP by the action of perbenzoic acid. Potassium permanganate on polycyclic rubber produces another oxide of the same composition but different solubility. These products are very interesting theoretically, because although the polycyclic rubber contains a smaller proportion of double bonds than does rubber, strong oxidizing materials open up not only the double bonds but also the newly formed cycles. Sulfur apparently does not do this but adds only to the double bonds.

The polycyclo-rubbers can be hydrogenated like rubber itself in the presence of a catalyst at high temperatures and pressures (85) (95). The hydro-polycyclo-rubbers are colorless, do not add bromine, and are stable toward hot nitric acid and potassium permanganate. The amount of hydrogen added, as determined by elementary analysis, corresponds to the unsaturation shown by other means.

Concentrated nitric acid reacts with polycyclo-rubber less energetically than with rubber but converts it into the same or a similar product. Long boiling with dilute nitric acid slowly de-

composes it, forming a water-soluble, nitrogen-containing acid, large amounts of hydrocyanic and oxalic acids, and unidentified products. In solution nitric acid forms what is probably a nitro-polycyclo-rubber, $(C_5H_7NO_2)_x$, as judged by its properties and the yield. It is more stable toward heat than is the corresponding derivative of rubber (see p. 111).

Structure. None of the derivatives or decomposition products have given any inkling as to the structure of the polycyclo-rubbers. Staudinger, working by analogy, has presented some results, however, which make it possible to build up a tentative scheme of the course of the reaction. He studied the action of zinc dust in the presence of hydrogen chloride on mono- and di-chloroparaffin hydrocarbons and terpenes, in which the chlorine was attached to a carbon atom to which a methyl group was also attached—a structure corresponding to the probable structure of rubber hydrochloride—and found that the chlorine was always split off as hydrogen chloride. 3-Ethyl-3-chlorononane, $C_{11}H_{23}Cl$, was converted into the corresponding undecene, $C_{11}H_{22}$, which has one double bond the position of which was not determined. 2,6-Dimethyl-2,6-dichloroheptane gave very interesting results; two equivalents of hydrogen chloride were removed and the compound was converted into alpha-cyclogeraniolene, the constitution of which is well known (212). The yield was 31.5 per cent.
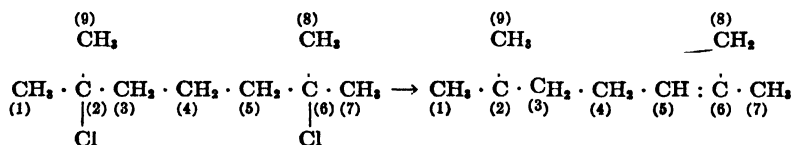
2,6-Dimethyl-2,6-dichloroheptane

α-Cyclogeraniolene

(For the sake of comparison, the numbering of the carbon atoms is the same as in the straight chain compound.)
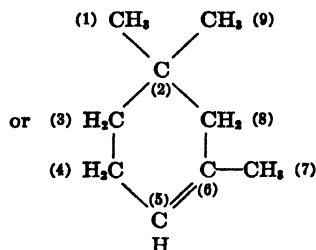
If the reaction is the same in the conversion of rubber hydro-chloride into polycyclo-rubber, then by analogy it can be represented as follows:

$$
\begin{array}{cccc}
CH_3 & CH_3 & CH_3 & CH_3 \\
| & | & | & | \\
\ldots CH_2 \cdot C \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CH_2 \ldots \rightarrow \\
| & | & | & | \\
Cl & Cl & Cl & Cl
\end{array}
$$

<div align="center">Rubber hydrochloride</div>

$$
\begin{array}{cccc}
CH_3 & CH_2 & CH_3 & CH_2 \\
| & | & | & | \\
\ldots CH_2 \cdot C \cdot CH_2 \cdot CH_2 \cdot CH:C \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CH_2 \cdot CH:C \cdot CH_2 \cdot CH_2 \ldots
\end{array}
$$
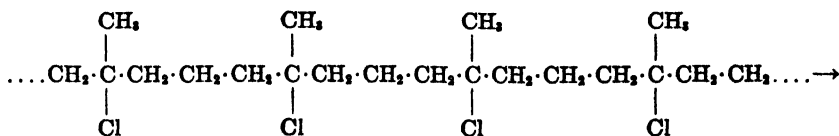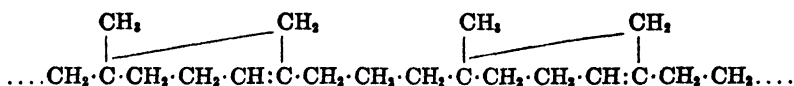
<div align="center">Polycyclo-rubber</div>

It is obvious that there are other possibilities in writing this structure, with the double bonds and the cycles in different positions, but this one gives a good analogous picture.

15. Vulcanization, acceleration and aging

Vulcanization, acceleration and aging are of the utmost importance in rubber technology, and yet at the present time complete chemical and physical explanations of them are not available. The practice generally precedes the theory, and, in this case, with the practice well developed, science apparently has a long way to go before it will provide complete explanations. The writer has no intention of going into a lengthy review of all the theories already set forth to explain these subjects, nor of propounding any new theories. He believes, however, that a résumé of the important contributions to these subjects would be worth while.

Vulcanization. When a mixture of rubber and sulfur is heated under proper conditions at "vulcanizing" temperatures, around 140°C., there takes place a gradual change from a plastic, tacky mixture to a very elastic, very strong, non-tacky product, which is familiar to all in the form of rubber bands, inner tubes, etc. In the industry this condition is designated as a good "cure." The early stages are known as "under cures," and the later stages, when the product on longer heating becomes weaker, as

"over cures." The most important difference between raw and vulcanized rubber is the increased resistance to plastic flow, or its permanent set. Properly vulcanized rubber, when stretched and allowed to return, goes back practically to its original shape, whereas raw rubber does not. Furthermore, this stretching and returning can be done many times without causing any particular change in the original shape. Too long heating produces a "reversion," and the product becomes softer and sometimes tacky, and on standing slowly "perishes." The time of heating for a good rubber-sulfur cure is about three hours, and such a vulcanizate will contain at least 2.5 per cent of combined sulfur. Weber (213), in order to make a proper comparison between combined sulfur and the rubber hydrocarbon in compounded stocks, suggested the use of a coefficient of vulcanization. This coefficient is an arbitrary number, being the percentage ratio of sulfur and the original rubber present. Vulcanizates, even of rubber and sulfur alone, do not necessarily have the same physical properties when the coefficients are the same. The rate of combination is the same, but the properties vary with the previous treatment of the rubber (214). Sulfur is soluble in both raw and vulcanized rubber (146), and the portion uncombined with the hydrocarbon, the "free" sulfur, slowly crystallizes out on the surface as a grayish powder, commonly known as "bloom."

The evidence for the chemical combination with sulfur is chiefly as follows: (1) that when extracted with a liquid which dissolves sulfur but not rubber—for example, acetone—the sulfur is not removed beyond a certain definite amount, this amount depending on the conditions under which the rubber was vulcanized (215) (216); (2) that when so extracted with acetone to remove the free sulfur, and then extracted with hot benzene, each fraction, dissolved and undissolved, contains the same proportion of combined sulfur as any other fraction and as the original (215) (217); (3) that there is no measurable transfer of sulfur when vulcanized rubber is heated with some raw rubber in solution (217); (4) that when raw rubber is heated in solution with as much as 1000 per cent excess of sulfur, the product contains no more combined sulfur than the amount required for saturation of the rubber

hydrocarbon as determined by other means, both chemical and physical (144); (5) that the amount of unsaturation of vulcanized rubber, as determined by the addition of bromine (147) and iodine chloride (148) corresponds to the difference between that which can be accounted for by the combined sulfur, using one atomic equivalent of sulfur for each C_5H_8 group, and the unsaturation of the original rubber; and (6) that the rate of chemical combination is regular, and the velocity coefficient of the reaction has been found to be 2.65 for 10 degrees increase in temperature, a value agreeing with that generally obtained in the case of a chemical reaction (214). The combined sulfur has never been removed from vulcanized rubber and the original rubber regenerated. In other words, rubber has never been completely devulcanized. Furthermore, completely saturated rubber, hydrorubber, is not affected by treatment with sulfur chloride (see p. 103). These facts leave no doubt that sulfur combines chemically with the rubber hydrocarbon, and they help to show that the theory of adsorption put forth by Wo. Ostwald (218) is untenable. Nevertheless, they do not explain all that constitutes vulcanization. A brief statement, therefore, of some of the other theories of vulcanization may not be amiss.

Brande (219), as far back as 1852, expressed the opinion that "the rubber acquires its new and distinct properties . . . . by the assumption of a new molecular condition; that, like phosphorus, it has assumed an allotropic state." Axelrod (220) postulated a depolymerization by the heat and a repolymerization by the sulfur, with simultaneous formation of a sulfur addition product. Kirchhof (221) regarded vulcanization as the transformation of rubber from a relatively unstable to a stable form, the chemical combination of sulfur being a subsidiary process. Ostromislenski (222) stated that "the process of vulcanization consists of two fundamental stages, (1) a chemical reaction in which only a small part of the rubber participates, and (2) an adsorption or swelling of the unchanged part of the rubber in the product of the chemical reaction." Harries's (223) theory resembled Kirchhof's. He thought of the raw rubber as a metastable form which passes into a stable form in the presence of sulfur,

and that the combination of sulfur is a secondary reaction or a post-vulcanization. Stevens (224) suggested that vulcanized rubber may consist of two phases, one the soft, unchanged, raw rubber, and the other the hard, tough, completely sulfurized compound, C_5H_8S, and that the latter is dispersed in the former. Twiss (225) likened these dispersed rubber sulfide particles to particles having reënforcing properties such as carbon black, etc., and this idea has been elaborated with further experimental evidence by Stevens (226); this viewpoint is contested by Boiry (227) who showed that mixtures of rubber and carbon black could be separated into fractions containing different proportions of carbon black. Stevens's most recent work (228) includes an account of experiments in which hard rubber is made at low temperatures, 100°C., by the use of ultra-accelerators, and vulcanized products are obtained containing coefficients of vulcanization much beyond 47, the coefficient for C_5H_8S.

Twiss (229) has investigated the vulcanizing action of the different modifications of sulfur, such as S_λ (ordinary crystalline sulfur), S_μ, and S_π, and has shown that the differences, if any, are small. Peachey (230) vulcanizes rubber at ordinary temperatures by forming the sulfur directly in the rubber through the action of hydrogen sulfide and sulfur dioxide, to which gases the rubber is exposed alternately. Some of the sulfur combines chemically. Such a vulcanization can also be carried out in solution, and Bedford and Sebrell (231) attribute the reactivity of the sulfur under these conditions to the formation of thiozone, following the earlier suggestion of Erdman (232) for regular sulfur vulcanization. Romani (233), working in Bruni's laboratory, discovered that rubber can be vulcanized with tetramethylthiuram disulfide, especially when zinc oxide is present. He believes that a form of active sulfur is split off from the disulfide. Helbronner and Bernstein (234) vulcanized rubber in solution in the presence of ultra-violet light. The dried films contained upwards of 0.78 per cent of combined sulfur. All the above methods use sulfur in some form or other (234a).

Ostromislenski (222), working on the theory that the vulcanizing agent is one which both adds to the double bond and

oxidizes it, discovered two new classes of agents, neither of which contains sulfur: the polynitrobenzenes, especially *m*-dinitrobenzene and 1,3,5-trinitrobenzene, and benzoyl peroxide. The polynitrobenzenes work with and without the presence of certain oxides, such as litharge, and the vulcanizates are comparable to those made with sulfur. The amounts used are only 0.5–2 parts with 100 parts of rubber. The benzoyl peroxide must usually be present up to about 10 parts, but no other ingredient is necessary. Ostromislenski states that the action is probably chiefly an oxidation. Fisher and A. E. Gray (235) found that the unsaturation of these vulcanizates was not changed from that of the original rubber, within the accuracy of the method employed. Therefore, if there is any oxidation it is very small in amount. It is possible, of course, that oxidation would not involve the double bonds, but this seems improbable. Oxygen and sulfur have many properties in common, and oxygen may act like sulfur in this case. If it does, then the amount necessary to cause the change is very small. If the above is correct, then by analogy ordinary vulcanization is a change in the hydrocarbon brought about by the sulfur, perhaps acting catalytically, and the chemical union of sulfur is a secondary reaction producing a further change which gives properties that are very important in the manufacture of rubber goods, but which is a change of degree only, not of kind. When the sulfur adds, it is not known whether an atom adds to a double bond forming an ethylene sulfide type, or whether two atoms unite with two double bonds forming a bridge either in the same molecule or between different molecules or aggregates.

It is not unreasonable to assume that the change is a type of polymerization. The relative decrease in unsaturation caused by the polymerization of such large units would be very small indeed, —probably too small to be measured by our present methods. Now, rubber itself is regarded as a polymerization product of isoprene, and isoprene can be polymerized into rubber-like products. In this polymerization the liquid isoprene is transformed into an elastic solid which is soluble in the rubber solvents but no longer soluble in many of the other solvents capable of dissolving isoprene itself. Moreover, some forms of synthetic rubber are ap-

parently so highly polymerized that they are practically insoluble in all organic solvents. It seems possible, therefore, that raw rubber may be further polymerized into a product that is more resistant to solvents than raw rubber itself, and it seems possible that such a change may be the same as that occurring during the first stage of vulcanization. An objection which may be raised to this idea is that the reverse of the process, depolymerization, has never been carried out, or, in other words, as stated above, rubber has never really been devulcanized (236) (217).

The question is quite open, and further work must be done to find out whether vulcanization is chiefly a polymerization, whether the method of combination of the sulfur causes the change, or whether the change is due to reaggregation, the dispersion of sulfur addition products, etc. Time will surely tell.

Reclaimed rubber, which is frequently spoken of commercially as "devulcanized" rubber, is manufactured not by removing the combined sulfur but by replasticizing old vulcanized rubber goods. The process in most general use is the Marks alkali process (237), which consists in heating the rubber under pressure with an aqueous solution of about 5 per cent of its weight of sodium hydroxide. It is then thoroughly washed, strained, and "refined" by milling. About 250,000 tons of reclaimed rubber were manufactured in the United States in 1929. Only about 60 per cent of this represents the original raw rubber, the other 40 per cent consisting of the compounding ingredients used in making the articles. Reclaimed rubber in rubber goods has a tendency to cause poor aging, but now with the use of antioxidants reclaimed rubber can be used to a far greater extent than formerly, and thus its use makes for a better economic condition.

Acceleration. Accelerators (237a) of vulcanization not only shorten the time of vulcanization, but also make it possible to use lower temperatures and to obtain products with enhanced physical properties and frequently with better aging qualities. Accelerators are used in small amounts, approximately 0.01 to 1.0 part with 100 parts of rubber. Zinc oxide is often necessary for proper activation of the accelerator. Inorganic accelerators such as litharge and magnesia have been known for a long time,

but organic accelerators, used commercially in 1906 by Oenslager, were first given to the world in the published patents of Bayer and Co. (238) in 1912. Oenslager used aniline and thiocarbanilide, and the Bayer patents disclosed the use of piperidine and its CS_2-addition product. The latter is typical of an "ultra-accelerator." In its presence rubber can be vulcanized in 2–3 minutes at 140°C., and also on standing for several weeks at ordinary temperatures. It will also gel a rubber cement containing sulfur and zinc oxide. Most organic accelerators contain nitrogen, some nitrogen and sulfur, and some, such as the xanthates, sulfur but no nitrogen. They apparently act by causing the formation of an active form of sulfur.

Aging. A rubber band around papers set aside in a drawer becomes hard and brittle, the side wall of an automobile tire becomes cracked and crumbly, the rubber covering of a raincoat allowed to remain in the sun on the beach changes to a sticky mass; these familiar changes are typical of the aging of vulcanized rubber. All rubber goods, however, do not deteriorate like these. The old red hot-water bottles and red rubber bands showed excellent keeping qualities, and on this account even to-day many people still think of rubber as being red. These articles were vulcanized with crimson antimony sulfide (a polysulfide), and for some little understood reason such articles age very well. Nowadays very little "crimson antimony" is used, but since people have been so used to the good aging qualities of the goods manufactured by its use, articles are made with a red dye added to imitate the color and an organic "age-resister" to assure proper keeping qualities. The short life of ordinary rubber goods has kept rubber from being used in many places where it would be of great assistance, especially in building operations, machines, etc., and now that its life can be prolonged considerably, whole new fields have been opened up.

Aging is the result of the action of air and light, separately or together. Only comparatively recently have chemists studied this question intensively, and they have found that certain chemicals can be added to rubber to prolong its life. These chemicals are termed "anti-agers," "age-resisters" or "antioxidants."

They are usually organic compounds, and the most useful have been the condensation products of aliphatic aldehydes and aromatic amines (acetaldehyde and aniline, and acetaldol and α-naphthylamine), and the phenyl naphthylamines. It is easy enough to test a chemical for its action as an accelerator of vulcanization because the time factor is small, but ordinary aging requires a long time. In order to provide an accelerated aging test, Geer (241) used an oven in which strips of rubber were hung and through which warm air, previously heated to 70°C., was passed. The strips of rubber were removed every other day during two weeks and tested for reduction of tensile strength and elongation. This method gives good predictions except for articles containing traces of copper or for those exposed to sunlight (242). Another method, and one very widely used today, is that devised by Bierer and Davis (243). The test pieces are kept in a bomb under 300 pounds pressure of oxygen and at about 70°C. This test is much shorter, does not predict sun cracking, and conclusions may also be drawn from the tensile strength and elongation.

A very fine review and bibliography of the subject is given by Kohman (244), together with much experimental work on the absorption of pure oxygen under constant, atmospheric pressure and constant temperature, 80°C. In the course of the absorption, the rubber first becomes tacky, then less tacky and dry, then weak and finally hard and brittle. The absorption of oxygen is autocatalytic in nature and appears to be both an addition and a decomposition reaction. Vulcanized rubber absorbs oxygen at a greater rate than raw rubber, and the rate of absorption increases with the degree of the cure. The deterioration is apparently proportional to the amount of oxygen absorbed, 0.5 per cent of oxygen decreasing the tensile strenth by nearly 50 per cent. The action of anti-agers is probably one of negative catalysis rather than of preferential absorption. The rate of oxygen absorption may be greatly retarded by their presence, and their effectiveness varies with their concentration and chemical constitution. Stretched rubber deteriorates much more rapidly than when at its original length (245). In ozone and sunlight it deteriorates most rapidly when stretched to 105–10 per cent. During the initial stage of

oxidation, the per cent of oxidation products increases much more rapidly than is indicated by the acetone extract, and on further oxidation, the products become insoluble in ether (246). Heating compounds in inert gases results at first in an increase in tensile strength because of a curing action, and then in a slow decrease which is insignificant as compared with the effect produced by oxygen.

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A REVIEW OF THE THEORY OF METALLIC CONDUCTION

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I. PROBLEM OF ELECTRICAL AND THERMAL CONDUCTION

The transport of electricity or of heat by metals is assumed to be effected principally through the agency of free electrons. These, under normal conditions of the metal, are assumed to be in statistical equilibrium, for which a distribution function f_0 exists, such that

$$f_0 (\xi, \eta, \zeta) \, d\xi \, d\eta \, d\zeta$$

gives the number of electrons per unit volume the velocity components of which lie between ξ and $\xi + d\xi$, η and $\eta + d\eta$, ζ and $\zeta + d\zeta$. It follows that n, the total number of electrons per unit volume, is given by the expression:

$$\int f_0 (\xi, \eta, \zeta) \, d\lambda;$$

in this expression $d\lambda$ is an element of the velocity-space equal to $d\xi d\eta d\zeta$, and the integration is to be extended over all values of the velocities. It follows also that, under normal conditions, the excess number of electrons passing (in the positive direction over the number passing in the negative direction) per second through a unit plane perpendicular to the direction corresponding with the ξ-component is

$$\int \xi f_0 (\xi, \eta, \zeta) \, d\lambda = 0 \tag{1}$$

Under the influence of a difference of potential or of a temperature gradient in the metal, the distribution function is altered,

$f(\xi, \eta, \zeta)$ replacing $f_0(\xi, \eta, \zeta)$, giving rise to a stream of electrons corresponding with the direction of the impressed force or of the temperature gradient. In the case of a difference of electrical potential applied in the direction of ξ, the current per unit cross-section is

$$J = e \int \xi f (\xi, \eta, \zeta) \, d\lambda, \qquad (2)$$

where e is the charge on the electron; correspondingly, in the case of a temperature gradient, the quantity of kinetic energy transferred per second per unit cross-section is

$$W = \frac{m}{2} \int v^2 \, \xi f (\xi, \eta, \zeta) \, d\lambda \qquad (2a)$$

where m is the mass of the electron and $v^2 = \xi^2 + \eta^2 + \zeta^2$.

In the absence of collisions, the electrons which at a given time are in the element of volume dS of the metal and the representative points of which in the velocity-space lie in $d\lambda$, after the lapse of time dt, are in an element of volume dS' of the metal, equal to dS, and their representative points in the velocity-space lie in $d\lambda'$, equal to $d\lambda$. The electrons of the group considered have initially the same components of velocity, or with only infinitesimal variations, since their representative points lie in $d\lambda$. Under the influence of a force giving rise to an acceleration X in the direction of the x-axis (i.e., the direction of ξ), operating during a time dt, ξ is altered to $\xi + Xdt$, x to $x + \xi dt$, y to $y + \eta dt$, z to $z + \zeta dt$; η and ζ remain unchanged. Since, in the absence of collisions, the number of electrons (reckoned per unit volume) characterized initially by $\xi, \eta, \zeta, x, y, z, t$ is equal to the number characterized, after the lapse of time dt, by the altered quantities just given, it follows necessarily that:

$$f (\xi, \eta, \zeta, x, y, z, t) = f (\xi + Xdt, \eta, \zeta, y + \eta \, dt, x + \xi \, dt, z + \zeta \, dt, t + dt) \quad (3)$$

During the passage of a group of electrons from $(dS, d\lambda)$ to $(dS', d\lambda')$, however, the number in the two groups does not in general remain the same on account of collisions. If b is the

number of electrons joining the group per second as a result of collisions and a the number leaving it, then

$$f\,(\xi,\,\eta,\,\zeta,\,x,\,y,\,z,\,t) + (b - a)\,dt = f\,(\xi + Xdt,\,\eta,\,\zeta,\,x + \xi\,dt,\,y + \eta\,dt,\,z + \zeta\,dt,\,t + dt) \quad (3a)$$

Since the right-hand side of equation (3a) may be replaced by:

$$f\,(\xi,\,\eta,\,\zeta,\,x,\,y,\,z,\,t) + \frac{\partial f}{\partial \xi}\,Xdt + \frac{\partial f}{\partial x}\,\xi\,dt + \frac{\partial f}{\partial y}\,\eta\,dt + \frac{\partial f}{\partial z}\,\zeta\,dt + \frac{\partial f}{\partial t}\,dt$$

and since the function f is assumed constant in y, z, t for a steady-state condition arising from a force in the x-direction, it follows that:

$$b - a = \frac{\partial f}{\partial \xi}\,X + \frac{\partial f}{\partial x}\,\xi \quad (4)$$

In order to simplify the calculation of $(b - a)$, the atoms are considered as rigid, elastic spheres; further, the atoms are considered as immovable on account of their relatively large masses, and the mutual collisions between electrons are ignored. The number of collisions between electrons of the group $(d\lambda)$ and metal atoms, such that the line of centers lies within a solid angle dw (equal to $\sin\vartheta\,d\vartheta\,d\varphi$) is first to be considered. ϑ is the angle between the line of centers (at the moment of impact) and the direction of the velocity of the electron (figure 1); φ is the dihedral angle between the plane POx (formed by the x-axis and a line drawn from the origin in the direction of the velocity) and the plane POQ (formed by two lines drawn from the origin of coördinates, one in the direction of the line of centers at impact, the other in the direction of the velocity). The velocity component in the direction of the line of centers at impact is $v\cos\vartheta$. Electrons colliding in the manner specified must lie at the moment of impact on a surface-element of a sphere, the radius R of which is equal to the sum of the effective radii of atom and electron. This surface-element is $R^2\sin\vartheta\,d\vartheta\,d\varphi$. All electrons of the group having positions at a given moment within a distance equal to $v\cos\vartheta$ collide in the manner specified during the ensuing unit of time. The volume therefore containing electrons colliding during a second in the specified manner is $R^2v\cos\vartheta\,\sin\vartheta\,d\vartheta\,d\varphi$ and since

there are $f(\xi, \eta, \zeta)d\lambda$ electrons per unit volume in the group, the number of such collisions per second by electrons of the group with one metal atom is

$$f\ (\xi\ \eta\ \zeta)\ d\lambda \cdot R^2\ v\ \cos\vartheta\ \sin\vartheta\ d\vartheta\ d\varphi$$

If there are n metal atoms per unit volume, the total number of collisions per unit volume per second by electrons specified by

FIG. 1. GEOMETRICAL RELATIONSHIPS AT IMPACT

ξ, η, ζ such that the angle between the line of centers at impact and the direction of the velocity lies within the solid angle dw is

$$n\ R^2\ v\ f\ (\xi,\ \eta,\ \zeta)\ d\lambda \cdot \cos\vartheta\ \sin\vartheta\ d\vartheta\ d\varphi \qquad (5)$$

The velocity-point of the deflected electron may be found by a consideration of the fact that the velocity-component parallel to the direction of the line of centers at impact is reversed, while that perpendicular to it persists. Reference to the simplified,

two-dimensional diagram of figure 2 (see p. 144) shows the nature of the results:

$$\angle\,1 + \angle\,2 + \angle\,3 = \frac{\pi}{2}$$

$$\angle\,1 + \angle\,2 \qquad = g$$

$$\angle\,2 + \angle\,3 \qquad = \vartheta' = \vartheta$$

whence

$$\angle\,2 = g + \vartheta - \frac{\pi}{2}$$

$$\sin \angle\,2 = \frac{\xi'}{v'} = \frac{\xi'}{v} = -\cos(g + \vartheta) = \sin g\,\sin\vartheta - \cos g\,\cos\vartheta \qquad (5a)$$

$$\alpha = \pi/2 - \vartheta$$

$$\alpha + g = \pi/2 + (g - \vartheta)$$

$$\sin(\alpha + g) = \frac{\xi}{v} = \cos(g - \vartheta) = \cos g\,\cos\vartheta + \sin g\,\sin\vartheta \qquad (5b)$$

From a comparison of equations (5b) and (5a), it follows that:

$$\frac{\xi'}{v} + \cos g\,\cos\vartheta = \frac{\xi}{v} - \cos g\,\cos\vartheta \qquad (6)$$

or,

$$\xi' = \xi - 2\,v\cos g\,\cos\vartheta \qquad (6a)$$

By analogy,

$$\eta' = \eta - 2\,v\cos h\,\cos\vartheta \qquad (7)$$

$$\zeta' = \zeta - 2\,v\cos i\,\cos\vartheta \qquad (8)$$

The angles g, h, i are those between the direction of the line of centers at impact and the three rectangular axes. The deductions just made reveal the fact that the electrons of group $(d\lambda)$, upon collision with metal atoms, become members of other groups

$(d\lambda')$ all having the same total energy as the group $(d\lambda)$, the new components of velocity being related to the old ones by equations (6a), (7), (8). This fact in turn leads to a method of calculating the number of reverse collisions by electrons of groups $(d\lambda')$ such that after collision their representative points lie with those of the undeflected electrons of group $(d\lambda)$. It follows from expres-
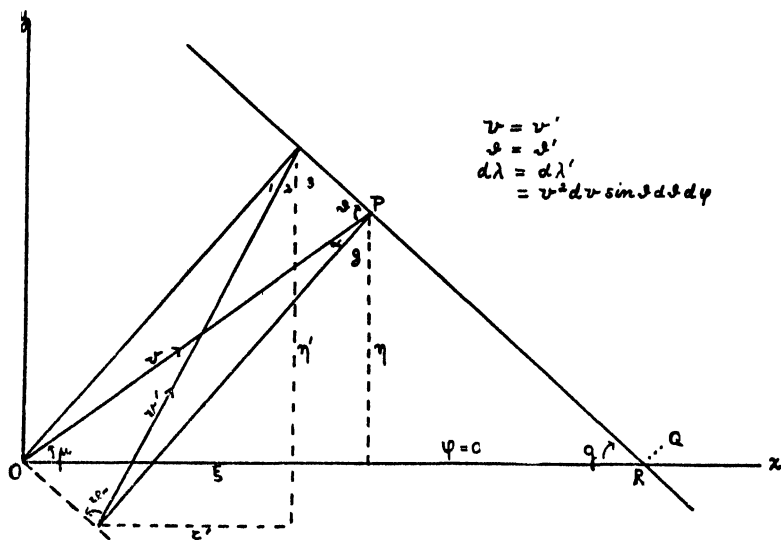
FIG. 2. DIAGRAM OF VELOCITIES

sion (5) that the number of *such* reverse collisions by electrons from a group $(d\lambda')$ such that the angle between the line of centers at impact and the direction of the velocity v' is ϑ' is

$$n \, R^2 \, f \, (\xi' \, \eta' \, \zeta') \, d \, \lambda' \, v' \, \cos\vartheta' \, \sin\vartheta' \, d\vartheta' \, d\varphi \tag{9}$$

$$(v' = v; \, \vartheta' = \vartheta; \, d\lambda' = d\lambda)$$

where the values of ξ', η', ζ' depend upon the orientation of the line of centers at impact. Hence,

$$b - a = n \, R^2 \, v \int_0^{\pi/2} \int_0^{2\pi} [f \, (\xi', \eta', \zeta') - f \, (\xi, \eta, \zeta)] \cos\vartheta \, \sin\vartheta \, d\vartheta \, d\varphi \tag{10}$$

and from equation (4),

$$n R^2 v \int_0^{\pi/2} \int_0^{2\pi} [f\ (\xi'\ \eta'\ \zeta') - f\ (\xi\ \eta\ \zeta)] \cos\vartheta\ \sin\vartheta\ d\vartheta\ d\varphi = X \frac{\partial f}{\partial \xi} + \xi \frac{\partial f}{\partial x} \quad (11)$$

A solution of the equation, in the form

$$f = f_0 + \xi \chi\ (v) \quad (12)$$

is to be tried, where f_0 is the normal distribution function and $\chi(v)$ an unknown function of the velocity alone. Substitution in (11) gives:

$$n R^2 v \chi\ (v) \int_0^{\pi/2} \int_0^{2\pi} (\xi' - \xi)\ \cos\vartheta\ \sin\vartheta\ d\vartheta\ d\varphi = X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \quad (13)$$

On the right-hand side of the preceding equation f_0 is used instead of the more exact $f_0 + \xi\chi(v)$. This procedure is permissible as an approximation, on account of the form of the expression and of the fact that f_0 is large in comparison with its perturbation. Obviously this approximation would be useless on the left-hand side of the equation. Substitution of the value of $(\xi' - \xi)$ from equation (6a) gives:

$$- 2 n R^2 v^2 \chi\ (v) \ |\ ^{/2} \int_0^{2\pi} \cos g\ \cos^2\vartheta\ \sin\vartheta\ d\vartheta\ d\varphi = X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \quad (14)$$

The line of centers at impact (PR...Q in figure 1) and the axis Ox are not necessarily in the same plane; g is the angle between these two lines. Ox is inclined to the line OP (the direction of v) at an angle μ. The line of centers is inclined to OP at an angle ϑ. φ is the dihedral angle between the plane (PR...Q and OP) and the plane of (Ox and OP); whence,

$$\cos g = \cos\mu\ \cos\vartheta + \sin\mu\ \sin\vartheta\ \cos\varphi \quad (15)$$

$$\left(\cos\mu = \frac{\xi}{v}\right).$$

Substitution in equation (14) gives:

$$- 2 n R^2 v^3 \chi\ (v) \int_0^{\pi/2} \int_0^{2\pi} (\cos\mu\ \cos\vartheta + \sin\mu\ \sin\vartheta\ \cos\varphi)\ \cos^2\vartheta\ \sin\vartheta\ d\vartheta\ d\varphi \quad (16)$$

The result of integration with respect to φ is:

$$- 4 \pi n R^2 v \chi (v) \xi \int_0^{\pi/2} \cos^3 \vartheta \sin \vartheta \; d\vartheta = X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \qquad (17)$$

integration with respect to ϑ gives:

$$- \pi n R^2 v \chi (v) \xi = X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \qquad (18)$$

The unknown function $\chi (v)$ is thus found to be:

$$\chi (v) = \frac{-l}{v \xi} \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) \qquad (18a)$$

in which l has been set equal to $\dfrac{1}{\pi n R^2}$. The essayed solution in which χ is assumed to depend upon v alone is thus found to be satisfactory since ξ itself disappears from the right-hand side of equation (18a) upon performing the indicated operations,

$$\left[\frac{1}{\xi} \frac{\partial}{\partial \xi} = \frac{1}{v} \frac{\partial}{\partial v} \right].$$

Hence, the distribution function describing the system is

$$f = f_0 - \frac{l}{v} \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) \qquad (19)$$

and by equation (2), the quantity of electricity J transported per second per unit cross-section is:

$$J = e \int \xi \left[f_0 - \frac{l}{v} \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) \right] d\lambda \qquad (20)$$

and by equation (1)

$$J = - e \int \frac{\xi \, l}{v} \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) d\lambda \qquad (21)$$

The quantity of heat W transported per second per unit cross-section is, similarly,

$$W = \frac{m}{2} \int v^3 \xi \left[f_0 - \frac{l}{v} \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) \right] d\lambda = - \frac{m}{2} \int \xi \, l \, v \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} \right) d\lambda \quad (21a)$$

II. APPLICATION OF CLASSICAL STATISTICS TO THE PROBLEM OF CONDUCTION

In so far as the assumptions and approximations of the last section, which constitutes essentially the treatment of Lorentz, are adequate to describe the phenomenon of conduction in metals, there remains only the choice of a normal distribution function f_0 and its application to formulas (21) and (21a) in order to obtain a final solution of the problem. The classical distribution function of Maxwell and Boltzmann was used by Lorentz and is easily obtained by commencing with the relationship accredited to Boltzmann connecting the entropy of a system with its thermodynamic probability. The latter quantity is defined as the number of microscopic complexions in a given collection all of which correspond to the same macroscopic state of the system. A given microscopic complexion is specified by means of the position coördinates and corresponding components of momenta of each of the molecules of the system. Varying numbers of microscopic complexions thus correspond with various macroscopic states, there being the maximum number of microscopic complexions in the equilibrium macroscopic state. The various microscopic complexions corresponding with a given macroscopic state differ by permutations of the individual molecules, the individuality of the molecules being insignificant as regards the macroscopic state. Boltzmann's relationship is

$$S = k \log W \qquad (22)$$

where S is the entropy, k a proportionality constant to be identified later, and W the thermodynamic probability corresponding with the state of the system giving rise to the entropy S. In order to specify the positions and momenta of the molecules it is

convenient to conceive a space of six dimensions, along three of the axes of which the space coördinates of the molecules are represented, and along the other three axes of which the coördinates of momenta are represented. This six-dimensional space (the phase-space) is divided into cells of equal magnitude; the magnitude of a cell is small in comparison with the entire space representing the system. A macroscopic state of a system is thus specified by N_1 molecules having representative points lying in cell 1, N_2 molecules in cell 2, ... N_s molecules in cell s. The number of ways in which this distribution can be realized by a system containing N molecules is:

$$W = \frac{N\,!}{N_1\,!\,N_2\,!\,\ldots\,N_s\,!};\qquad (23)$$

$$\sum_s N_s = N \qquad (24)$$

The total energy E is accordingly:

$$E = \sum_s \epsilon_s N_s$$

where ϵ_1, ϵ_2, . . . ϵ_s are the energies characteristic of the cells 1, 2, . . . s, and the summations are taken so as to include all of the cells of the phase-space. If the distribution is an equilibrium one, then it gives rise to the maximum entropy; or

$$\frac{1}{k}\,\delta\,S = \delta \log W = 0 \qquad (25)$$

for *any* arbitrary, small variation in the equilibrium. If the system contains a constant number of molecules and a constant energy, it follows that

$$\delta N = \sum_s \delta N_s = 0 \qquad (26)$$

$$\delta E = \sum_s \epsilon_s \delta N_s = 0 \qquad (27)$$

as subsidiary conditions on the arbitrary variation in the equilibrium. By an application of Stirling's formula,

$$\log x\,! = x \log x - x,$$

it follows from equation (23) that:

$$\log W = N \log N - N - \Sigma_s N_s \log N_s + \Sigma_s N_s \qquad (28)$$

and

$$\delta \log W = - \Sigma_s (\log N_s + 1) \, \delta N_s = 0 \qquad (29)$$

The subsidiary conditions, $\delta N = 0$ and $\delta E = 0$, rob two of the δN's of their independence. Thus any variation, subject to the imposed conditions, involves at least three cells:

$$-\frac{1}{k} \delta S = (\log N_1 + 1) \, \delta N_1 + (\log N_2 + 1) \, \delta N_2 + (\log N_3 + 1) \, \delta N_3 = 0 \quad (30)$$

$$\delta N = \qquad\qquad \delta N_1 + \qquad\qquad \delta N_2 + \qquad\qquad \delta N_3 = 0 \quad (31)$$

$$\delta E = \qquad\qquad \epsilon_1 \delta N_1 + \qquad\qquad \epsilon_2 \delta N_2 + \qquad\qquad \epsilon_3 \delta N_3 = 0 \quad (32)$$

These equations may be solved by finding quantities α and β by which equations (31) and (32) respectively are to be multiplied, such that upon addition of the three equations the coefficients of δN_1 and δN_2 vanish. Then

$$(\log N_3 + 1 + \alpha + \beta \, \epsilon_3) \, \delta N_3 = 0$$

and since

$$\delta N_3 \neq 0$$

$$(\log N_3 + 1 + \alpha + \beta \, \epsilon_3 = 0$$

$$N_3 = e^{-1-\alpha-\beta \epsilon_3} = A \, e^{-\beta \epsilon_3}$$

where A is a constant.

If cells 2, 3, and s are now chosen for the arbitrary variation, with the same multipliers α and β, the coefficients of δN_2 and δN_3 vanish, and hence that of δN_s; or

$$N_s = A \, e^{-\beta \epsilon_s} \qquad (33)$$

The constants α and β can be determined from a formal comparison of thermodynamic quantities with the equations themselves:

$$-\frac{1}{k}\, \delta\, S \,=\, 0$$

$$\alpha\, \delta\, N \,=\, 0$$

$$\beta\, \delta\, E \,=\, 0$$

$$\frac{\cdot}{k}\, \delta\, S \,-\, \alpha\, \delta\, N \,-\, \beta\, \delta\, E \,=\, 0$$

If partial differential coefficients, at constant volume, are formed, it follows that:

$$\frac{1}{k}\left(\frac{\partial S}{\partial E}\right)_{V,\,N} = \beta; \tag{34}$$

$$\frac{1}{k}\left(\frac{\partial S}{\partial N}\right)_{E,\,V} = \alpha \tag{35}$$

From the definition of the change in entropy of a given quantity of matter:

$$dS \qquad \frac{dE + p\, dV}{} \tag{36}$$

where T is the absolute temperature and p the pressure. It follows that

$$\beta = \frac{}{kT} \tag{37}$$

The coefficient $\left(\dfrac{\partial S}{\partial N}\right)_{E,\,V}$ may be found by considering the entropy as a function of the three independent variables $E,\ V,\ N$.

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,\,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,\,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,\,V} dN \tag{38}$$

By means of (36),

$$dS = \frac{1}{T}\, dE + \frac{p}{T}\, dV + \left(\frac{\partial S}{\partial N}\right)_{E,\,\cdot} dN \tag{39}$$

$$\left[\frac{\partial}{\partial N}(TS - E - pV)\right]_{T,p} \equiv -\left(\frac{\partial F}{\partial N}\right)_{T,p} = T\left(\frac{\partial S}{\partial N}\right)_{E,V} = \alpha\,k\,T \quad (40)$$

or

$$\alpha = -\frac{\zeta}{k\,T} \quad (41)$$

where ζ is the chemical potential, i.e., the "partial molal" free energy (reckoned per molecule). Had the partial differential coefficients been taken at constant pressure instead of at .constant volume, the significance of both α and β would have been altered, but altered in a manner such as not to affect equation (33); for the system of equations (33) determines the maximum entropy, and with constant N, E, and V the entropy, as well as pressure, etc., is fixed.

The following equations serve for the determination of the constants A and k:

$$N = \Sigma_s N_s = A \Sigma_s e^{-\beta \epsilon_s} = A \int e^{-\frac{\epsilon}{k\,T}} dp_x\, dp_y\, dp_z \quad (42)$$

$$E = \Sigma_s N_s \epsilon_s = A \Sigma_s \epsilon_s e^{-\beta \epsilon_s} = A \int \epsilon\, e^{-\epsilon/k\,T} dp_x\, dp_y\, dp_z \quad (43)$$

where p_x, p_y, p_z are components of momentum corresponding with the energy ϵ. If the energy is wholly kinetic,

$$\frac{1}{2} m\, v^2 = \epsilon \quad (44)$$

$$m\, v\, dv = d\epsilon \quad (45)$$

$$v^2\, dv = \frac{\sqrt{2}}{m^{3/2}} \sqrt{\epsilon}\, d\epsilon \quad (46)$$

Also

$$dp_x\, dp_y\, dy_z = m^3\, d\xi\, d\eta\, d\zeta = m^3\, v^2\, dv\, \sin\vartheta\, d\vartheta\, d\varphi \quad (47)$$

where ϑ, φ are angles determining the direction of the velocity in spherical polar coördinates.

Whence:

$$N = \sqrt{2}\, A\, m^{3/2} \int_{\epsilon=0}^{\epsilon=\infty} \int_{\vartheta=0}^{\vartheta=\pi} \int_{\varphi=0}^{\varphi=2\pi} e^{-\frac{\epsilon}{kT}} \sqrt{\epsilon}\, d\epsilon \, \sin\vartheta \, d\vartheta \, d\varphi =$$

$$2^{5/2} \pi A\, m^{3/2} \int_0^\infty e^{-\frac{\epsilon}{kT}} \sqrt{\epsilon}\, d \qquad (48)$$

$$E = \sqrt{2}\, A\, m^{3/2} \int_{\epsilon=0}^\infty \int_{\vartheta=0}^\pi \int_{\varphi=0}^{2\pi} e^{-\frac{\epsilon}{kT}} \epsilon^{3/2}\, d\epsilon \, \sin\vartheta \, d\vartheta \, d\varphi =$$

$$2^{5/2} \pi A\, m^{3/2} \int_0^\infty e^{-\frac{\epsilon}{kT}} \epsilon^{3/2}\, d\epsilon \qquad (49)$$

$$\int_0^\infty e^{-\frac{\epsilon}{kT}} \epsilon^n \, d\epsilon = (kT)^{n+1}\, \Gamma(n+1)$$

$$\Gamma(3/2) = \frac{1}{2}\sqrt{\pi}$$

$$\Gamma(5/2) = \frac{3}{4}\sqrt{\pi}$$

$$N = (2\pi m k T)^{3/2}\, A; \quad A = \frac{N}{(2\pi m k T)^{3/2}} \qquad (50)$$

$$E = \frac{N}{(2\pi m k T)^{3/2}} (kT)^{5/2} \cdot \frac{3}{2} \cdot (2\pi m)^{3/2} = \frac{3}{2} N k T \qquad (51)$$

The heat capacity of the gas,

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \frac{3}{2} N k \qquad (52)$$

Whence by comparison with experiment,

$$k = \frac{R}{N}$$

where R is the molar gas constant.

On the basis of classical statistics, therefore, it follows that the

number of molecules having components of momentum lying between p_z and $p_z + dp_z$, p_y and $p_y + dp_y$, p_z and $p_z + dp_z$ is:

$$\frac{N}{(2 \pi m k T)^{3/2}} e^{-\frac{(p_x^2 + p_y^2 + p_z^2)}{2 m k T}} dp_x \, dp_y \, dp_z \qquad (53)$$

where N is the total number of molecules. The number having given velocity components is:

$$N \left(\frac{m}{2 \pi k T}\right)^{3/2} e^{-\frac{m}{2 k T}(\xi^2 + \eta^2 + \zeta^2)} d\xi \, d\eta \, d\zeta \qquad (54)$$

and the number having a velocity of magnitude v is

$$4 \pi N \cdot \left(\frac{m}{2 \pi k T}\right)^{3/2} e^{-\frac{m v^2}{2 k T}} v^2 \, dv \qquad (55)$$

The distribution function f_0 appropriate for application in equations (21) and (21a) is thus:

$$f_0 = A' e^{-b v^2}$$

where

$$A' = \frac{N}{V} \left(\frac{m}{2 \pi k T}\right)^{3/2} = n \left(\frac{m}{2 \pi k T}\right)^{3/2}$$

and

$$b = \frac{m}{2 k T}$$

Equations (21) and (21a) for the quantities of electricity and of heat, respectively, transferred through unit cross-section per second are:

$$J = - e \int \frac{\xi \cdot l}{v} \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x}\right) d\xi \, d\eta \, d\zeta \qquad (21)$$

$$W = - \frac{m}{2} \int \xi \cdot l \cdot v \left(X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x}\right) d\xi \, d\eta \, d\zeta \qquad (21a)$$

$$\frac{\partial f_0}{\partial \xi} = -2 A' b e^{-b v^2} \xi$$

$$\frac{\partial f_0}{\partial x} = \left[\frac{\partial A'}{\partial x} - A' v^2 \frac{\partial b}{\partial x}\right] e^{-b v^2}$$

$$X \frac{\partial f_0}{\partial \xi} + \xi \frac{\partial f_0}{\partial x} = -\xi e^{-b v^2} \left(2 A' b X - \frac{\partial A'}{\partial x} + A' v^2 \frac{\partial b}{\partial x}\right) \qquad (56)$$

Whence

$$J = e \cdot l \int \xi^2 e^{-b v^2} \left(\frac{2 A' b X}{v} - \frac{1}{v}\frac{\partial A'}{\partial x} + A' v \frac{\partial b}{\partial x}\right) d\xi \, d\eta \, d\zeta \qquad (57)$$

$$W = \frac{m \cdot l}{2} \int \xi^2 e^{-b v^2} \left(2 A' b X v - v \frac{\partial A'}{\partial x} + A' v^3 \frac{\partial b}{\partial x}\right) d\xi \, d\eta \, d\zeta \qquad (57a)$$

ξ^2 may be replaced by $\dfrac{v^2}{3}$, $d\xi \, d\eta \, d\zeta$ by $4 \pi v^2 \, dv$, and v^2 by q, whence

$$J = \frac{4 \pi e l}{3} \int_0^\infty e^{-b q} \left(A' b X q - \frac{1}{2}\frac{\partial A'}{\partial x} q + \frac{A'}{2}\frac{\partial b}{\partial x} q^2\right) dq \qquad (58)$$

$$2 \pi l m \int_0^\infty e^{-b q} \left(A' b X q^2 - \frac{1}{2}\frac{\partial A'}{\partial x} q^2 + \frac{A'}{2}\frac{\partial b}{\partial x} q^3\right) dq \qquad (58a)$$

$$\int_0^\infty e^{-b q} q^n \, dq = \frac{n!}{b^{n+1}}$$

if n is an integer. Whence

$$J = \frac{4 \pi e l}{3} \left(\frac{A' X}{b} - \frac{1}{2 b^2}\frac{\partial A'}{\partial x} + \frac{A'}{b^3}\frac{\partial b}{\partial x}\right) \qquad (59)$$

$$W = \frac{2 \pi l m}{3} \left(\frac{2 A' X}{b^2} - \frac{1}{b^3}\frac{\partial A'}{\partial x} + \frac{3 A'}{b^4}\frac{\partial b}{\partial x}\right) \qquad (59a)$$

The coefficient of electrical conductivity σ, under the condition of constant temperature throughout the conductor $\left(\dfrac{\partial A'}{\partial x} = 0,\right.$

$\dfrac{\partial b}{\partial x} = 0\Big)$, is easily obtained from equation (59). The acceleration X is given by $\dfrac{eE}{m}$ where E is the electric intensity. Whence, the value obtained by Lorentz:

$$\frac{J}{E} = \frac{4\,\pi}{3}\,\frac{e^2\,l\,A'}{m\,b}$$

$$\stackrel{'}{.} = n\left(\frac{m}{2\,\pi\,k\,T}\right)^{3/2}\cdot\frac{2\,k\,T}{m} = \frac{n}{\pi^{3/2}}\sqrt{\frac{m}{2\,k\,T}}$$

$$^{\text{\tiny u}} - \frac{e^2\,l\,n}{3\sqrt{2\,\pi\,m\,k\,T}} \tag{60}$$

The coefficient of thermal conductivity in a conductor in which there is no flow of electricity can be obtained from equation (59a) by utilizing the relationship $J = 0$ from equation (59).

$$J = 0 = \frac{4\,\pi}{3}\,e\,l\left(\frac{A'\,X}{b} - \frac{1}{2\,b^2}\,\frac{\partial A'}{\partial x} + \frac{A'}{b^3}\,\frac{\partial b}{\partial x}\right) \tag{61}$$

whence

$$\frac{2\,A'\,X}{b^2} \qquad \frac{1}{b^3}\,\frac{\partial A'}{\partial x} \qquad \frac{2\,A'}{b^4}\,\frac{\partial b}{\partial x} \tag{62}$$

Substitution by means of this equation in equation (59a) gives

$$W = \frac{2\,\pi}{3}\,l\,m\,\frac{A'}{b^4}\,\frac{\partial b}{\partial x} \tag{63}$$

$$\frac{\partial b}{\partial x} = \frac{\partial b}{\partial T}\,\frac{\partial T}{\partial x} = -\frac{m}{2\,k\,T^2}\,\frac{\partial T}{\partial x} \tag{64}$$

$$\frac{A'}{b^4} = \frac{n}{\pi^{3/2}}\left(\frac{2\,k\,T}{m}\right)^{5/2}$$

or,

$$W = -\frac{8}{3}\,\frac{l\,n\,k^2\,T}{\sqrt{2\,\pi\,m\,k\,T}}\,\frac{\partial T}{\partial x} \tag{65}$$

If the coefficient of thermal conductivity κ is defined by the equation

$$W = - \kappa \frac{\partial T}{\partial x} \tag{66}$$

the value obtained by Lorentz follows from comparison:

$$\kappa = \frac{8}{3} \frac{l\, n\, k^2\, T}{\sqrt{}} \tag{67}$$

and

$$\frac{\kappa}{\sigma} = 2 \left(\frac{k}{e}\right)^2 T = 0.165 \times 10^{-12}\, T.$$

The ratio has the value 4.8×10^{-11} for a temperature of 291°K. Experimental values for the ratio $\frac{\kappa}{\sigma}$ for common metals show a proportionality with T, and at a temperature of 291°K have approximately the value 7×10^{-11}. In the application of formulas such as (60) or (67), the quantity l, which is of the nature of a mean free path, is to be treated as an adjustable constant. For silver, as an example, if the number of free electrons is assumed to be equal to the number of metal atoms, the experimental value of σ (1/1600 in c.g.s. units) in equation (60) leads to a value of l equal to 4.7×10^{-7} cm. The assumption just made regarding the number of free electrons leads, on the basis of classical statistics, to a heat capacity contribution to the metal of $\frac{3}{2} Nk$, and even though the heat capacity of the electron-gas of the metal cannot be measured, theoretical evidence concerning the heat capacity of metals points towards a very inconsequential contribution from the electrons. Thus, in accordance with the theory presented, it is necessary, in order to explain satisfactorily the experimental values of σ, to assume that the number of free electrons is approximately equal to the number of metal atoms. This assumption in turn leads to an absurdly large contribution to the heat capacity.

III. APPLICATION OF THE NEW STATISTICS TO THE PROBLEM OF CONDUCTION

In the new systems of statistics, as developed either by Bose and Einstein or by Fermi, the fundamental postulate of Boltzmann relating entropy to thermodynamic probability is retained, but the method of calculating the thermodynamic probability is altered. As in the classical statistics, a phase-space is conceived for describing a system and is divided into cells of equal magnitude h^f, where h is Planck's constant and f the number of degrees of freedom of the molecule. In the development of classical statistics as given in section II of this article, the magnitude of the cells was not specified; nor was it necessary for the application there made. It would have been necessary there, however, had a numerical calculation of the entropy been attempted, but such an attempted calculation would have revealed an inconsistency in the calculation of the thermodynamic probability, forcing an "ad hoc" revision but not affecting the form of the distribution function. Besides removing the inconsistency just mentioned, the new systems of statistics, and especially the system developed by Fermi, appear to have a deeper physical basis than does the classical statistics. The statistics of Bose and Einstein and of Fermi both lead to essentially the same distribution function as classical statistics for gases at high temperatures and low densities. There are marked departures however in the case of gases under conditions such that the ratio of the temperature to the number of molecules per cubic centimeter $\frac{T}{n}$ is comparatively low. A gas in such a state is said to be degenerate. The conception of the free electrons in a metal as a gas and the assumption that the number of free electrons is equal to the number of metal atoms necessitate an extremely large value for n, as compared with gases under ordinary conditions of temperature and pressure; even for comparatively high temperatures, the ratio $\frac{T}{n}$ is so low that the electron-gas is in a highly degenerate state. Hence it is to be expected that the new statistics in its

application to the problem of conduction should lead to results very different from those of the classical theory.

According to the new statistics, a given state of a system (corresponding with a region of the phase-space containing Δs cells, all representing the same energy but different positions) is characterized by

$p_0 \Delta s$ cells being empty

$p_1 \Delta s$ cells containing one molecule

$\vdots$

$p_r \Delta s$ cells containing r molecules

$$\Sigma \, p_r = 1$$

The number of ways in which the given distribution can be realized, it being assumed that cells but not molecules have "identity," is:

$$W_{\Delta s} \quad \frac{\Delta s \, !}{(p_0 \, \Delta s) \, ! \, (p_1 \, \Delta s) \, ! \, \ldots \ldots \, (p_r \, \Delta s) \, !} \tag{69}$$

and $W_{\Delta s}$ is interpreted as the thermodynamic probability corresponding with the selected region of the phase-space. By Stirling's formula:

$$\log W_{\Delta s} = \Delta s \log \Delta s - \Delta s - \underset{r}{\Sigma} \, p_r \, \Delta s \log (p_r \, \Delta s) + \Sigma \, p_r \, \Delta s$$

$$= \Delta s \log \Delta s - \Delta s \underset{r}{\Sigma} \, p_r \log p_r - \Delta s \log \Delta s$$

$$= - \Delta s \underset{r}{\Sigma} \, p_r \log p_r \tag{70}$$

The logarithm of the probability per cell in the Δs-region is therefore

$$- \underset{r}{\Sigma} \, p_r \log p_r,$$

and the entropy of the entire system is

$$S = k \log W = - k \underset{s}{\Sigma} \underset{r}{\Sigma} \, p_r^s \log p_r^s \tag{71}$$

The summation with respect to r, according to the statistics of Bose and Einstein, runs from $r = 0$ to $r = \infty$ and, according to the statistics of Fermi, from $r = 0$ to $r = 1$, (i.e., a cell is either empty or contains one molecule). The summation with respect to s includes all cells of the phase-space of the system, compatible with its energy and volume. The quantities p_r^s etc. are to be interpreted as the probability that the sth cell contains r molecules, etc., in the sense that $\sum_r p_r^s r$ gives the average number of molecules in the sth cell, $\sum_r p_r^{s+1} r$ the average number in the $(s + 1)^{th}$ cell, etc.

In order to find the equilibrium distribution of a given system, it is necessary to render the entropy S a maximum, subject to the conditions of a constant number of molecules and constant energy. In accordance with the preceding notation the total number of molecules and the total energy are respectively:

$$N = \sum_s N_s = \sum \sum p_r^s r \tag{72}$$

$$E = \sum_s N_s \epsilon_s = \sum_s \sum_r \epsilon_s p_r^s r \tag{73}$$

where $\epsilon_1, \epsilon_2, \ldots \epsilon_s$ are the energies characteristic of the cells $1, 2 \ldots s$. The entropy is rendered a maximum by setting δS equal to zero for any, arbitrary, small variation of the quantities governing the distribution; i.e.,

$$-\frac{1}{k} \delta S = - \delta \log W = \sum_s \sum_r (\log p_r^s + 1) \, \delta \, p_r^s = 0 \tag{74}$$

Likewise, in order that N and E be constants during the variation:

$$\delta N = \sum_s \delta N_s = \sum_s \sum_r r \, \delta \, p_r^s = 0 \tag{75}$$

$$\delta E = \sum_s \epsilon_s \delta N_s = \sum_s \sum_r \epsilon_s r \, \delta \, p_r^s = 0 \tag{76}$$

and further, since

$$\sum p_r^s = 1$$

$$\Sigma \; \Sigma \; \delta \; p_r^s = 0 \tag{77}$$

With three subsidiary equations restricting the general variation, three δp's are robbed of their independence, and hence *any* variation, subject to the imposed conditions, involves at least four p's. By an application of an exactly similar method as that used for the corresponding problem in the classical statistics; i.e., by finding quantities α, β, γ by which equations (75), (76), (77) respectively are to be multiplied, such that upon addition of the four equations, (74) (75) (76) (77), the coefficients of three of the four δp's vanish, it follows that, since the fourth δp cannot be zero, its coefficient must vanish, or

$$p_r^s = e^{-1 - \gamma_s - (\alpha + \beta \epsilon_s) r} \tag{78}$$

The constant γ (requiring a subscript) can be determined at once from the relationship:

$$\Sigma_r \; p_r^s = 1 = e^{-1 - \gamma_s} \; \Sigma_r \; e^{-(\alpha + \beta \epsilon_s) r} \tag{79}$$

$$e^{-1 - \gamma_s} = \frac{1}{\displaystyle\Sigma_r \; e^{-(\alpha + \beta \epsilon_s) r}} \tag{80}$$

In the statistics of Bose and Einstein, $r = 0, 1, \ldots \infty$, whence,

$$e^{-1 - \gamma_s} = 1 - e^{-(\alpha + \beta \epsilon_s)} \tag{81}$$

and in the statistics of Fermi, $r = 0, 1$, whence,

$$e^{-1 - \gamma_s} = \frac{1}{- (\alpha + \beta \epsilon_s)} \tag{82}$$

The constants α, β, by reference to equations (41) and (37) and to their mode of introduction in equations (75) and (76) are recognized respectively as $-\dfrac{\bar{f}}{kT}$ and $\dfrac{1}{kT}$. For a pure gas, the free energy $(F = N\bar{f})$ is thus

$$F = E + pV - TS = -NkT\alpha \tag{83}$$

The number of molecules in any cell s is, according to the statistics of Bose and Einstein, found from equations (72), (78) and (81) to be:

$$N_s = \sum_{r=0}^{r=\infty} p_r^s \, r = \left[1 - e^{-(\alpha + \beta \epsilon_s)}\right] \sum_r r \, e^{-(\alpha + \beta \epsilon_s) r} = \frac{1}{e^{\alpha + \beta \epsilon_s} - 1} \quad (84)$$

and, according to the statistics of Fermi, from equations (72), (78) and (82):

$$N_s = \sum_{r=0}^{r=1} p_r^s \, r = \left[\frac{1}{1 + e^{-(\alpha + \beta \epsilon_s)}}\right] \sum_{0,1} r \, e^{-(\alpha + \beta \epsilon_s) r} = \frac{1}{e^{\alpha + \beta \epsilon_s} + 1} \quad (85)$$

The total number of molecules and the total energy are respectively:

$$N = \Sigma N_s = \sum_s \frac{1}{e^{\alpha + \beta \epsilon_s} \mp 1} \quad (86)$$

$$E = \Sigma N_s \, \epsilon_s = \sum_s \frac{\epsilon_s}{e^{\alpha + \beta \epsilon_s} \mp 1} \quad (87)$$

From equations (71) and (78), it follows that the entropy is:

$$S = - k \sum_s \sum_r p_r^s \, [- \alpha r - \beta \epsilon_s r \pm \log (1 \mp e^{-(\alpha + \beta \epsilon_s)})] \quad (88)$$

where, in the cases of alternation in sign, the upper sign is to be read for the statistics of Bose and Einstein and the lower one for the statistics of Fermi.

$$\sum_s \sum_r p_r^s \, r \, \alpha = N \alpha; \quad \sum_s \sum_r p_r^s \, \epsilon_s \, r \, \beta = \beta E$$

whence

$$S = N k \alpha + k \beta E \mp k \sum_s \log (1 \mp e^{-(\alpha + \beta \epsilon_s)}) \quad (89)$$

and since

$$F = - N k T \alpha, \quad \beta = \frac{1}{k T},$$

it follows that

$$S = -\frac{F}{T} + \frac{E}{T} \mp k \sum_s \log (1 \mp e^{-(\alpha + \beta \epsilon_s)}) \qquad (90)$$

By reference to the thermodynamic definition of F, it follows that

$$\frac{pV}{T} = \mp k \sum_s \log (1 \mp e^{-\alpha - \beta \epsilon_s}) \qquad (91)$$

It is immediately evident from equation (85) that, if the gas is in a state such that

$$e^\alpha = \frac{1}{A} \gg 1,$$

the distribution function of Bose and Einstein, or of Fermi, becomes essentially $A\ e^{-\beta \epsilon_s}$

$$(A \sum e^{-\beta \epsilon_s} = \sum N_s = N) \qquad (92)$$

and is therefore as regards form in accord with the classical theory. Furthermore, with the condition that $e^\alpha \gg 1$,

$$\frac{pV}{kT} = \mp \sum_s \log (1 \mp e^{-\alpha - \beta \epsilon_s}) \cong \mp \sum_s \mp e^{-\alpha - \beta \epsilon_s} = \sum_s A\ e^{-\beta \epsilon_s} = N \quad (93)$$

and by comparison with the experimental equation $pV = RT$, k is identified with $\dfrac{R}{N}$, R being the molar gas constant.

The constant $A(= e^{-\alpha})$ can be determined from equation (92) by replacing the sum by the corresponding integral:

$$\sum_s A\ e^{-\beta \epsilon_s} = A \int \ldots \int e^{-\beta \epsilon} \frac{dp_x\ dp_y\ dp_z\ dx\ dy\ dz}{h^3} \qquad (94)$$

The magnitude of a cell in the phase-space is thus assumed to be sufficiently small that for the purpose of integration it may be identified with $dp_x dp_y dp_z dx dy dz$. The integrations extend over all values of p_x, p_y, p_z consistent with the energy and over all

values of x, y, z consistent with the volume. As in equations (44) etc.,

$$\int \int \int dx \, dy \, dz = \int dV = V$$

$$dp_x \, dp_y \, dp_z = m^3 \, d\xi \, d\eta \, d\zeta = m^3 \, v^2 \, d\,v \, \sin\vartheta \, d\vartheta \, d\varphi = m^{3/2} \sqrt{2\,\epsilon} \, d\epsilon \, \sin\vartheta \, d\vartheta \, d\varphi$$

$$m^{3/2} \sqrt{2\,\epsilon} \, d\epsilon \int_{\vartheta\,=\,0}^{\vartheta\,=\,\pi} \int_{\varphi\,=\,0}^{\varphi\,=\,2\pi} \sin\vartheta \, d\vartheta \, d\varphi = 2^{5/2} \, \pi \, m^{3/2} \sqrt{\epsilon} \, d\epsilon$$

whence from equation (94),

$$N = \frac{A \cdot 2^{5/2} \, \pi \, V \, m^{3/2}}{h^3} \int_0^\infty e^{-\frac{\epsilon}{kT}} \sqrt{\epsilon} \, d\epsilon = \frac{(2 \, \pi \, m \, k \, T)^{3/2} \, A \, V}{h^3} \quad (95)$$

it being legitimate to extend the upper limit to ∞ on account of the form of the function. It follows that

$$A = \frac{N}{V} \frac{h^3}{(2 \, \pi \, m \, k \, T)^{3/2}} = n \cdot \frac{h^3}{(2 \, \pi \, m \, k \, T)^{3/2}} \quad (96)$$

The condition of non-degeneracy (i.e., $e^\alpha = \dfrac{1}{A} \gg 1$), in which case the form of the new distribution function does not differ essentially from the classical, is therefore that

$$\frac{n \, h^3}{(2 \, \pi \, m \, k \, T)^{3/2}} \ll 1 \quad (97)$$

For helium gas at 273°K and one atmosphere pressure

$$A \cong 4 \times 10^{-6} \ll 1 \left(\begin{array}{l} n = \dfrac{6.06 \times 10^{23}}{22,400} \\[2mm] m = \dfrac{4}{6.06 \times 10^{23}} \end{array} \right.$$

while for the free electrons in silver at 300°K

$$A \cong 0.5 \times 10^4 \gg 1 \left(\begin{array}{l} n = \dfrac{d}{M} \times 6.06 \times 10^{23} \\[2mm] m = 9.02 \times 10^{-28} \end{array} \right.$$

Accordingly, the free energy of a non-degenerate gas by equation (83) is:

$$F_a = - N k T \alpha = N k T \log A = N k T \log \left[\frac{N}{V} \frac{h^3}{(2 \pi m k T)^{3/2}} \right] \quad (98)$$

$$V = \frac{N k T}{p}$$

whence, the entropy of a non-degenerate gas is:

$$S = - \left(\frac{\partial F}{\partial T} \right)_p = N k \log \left[\frac{(2 \pi m k T)^{3/2} e^{5/2} V}{N h^3} \right] \quad (99)$$

This theoretical value for the entropy of a monatomic gas corresponds closely with experimental results (based on the third law of thermodynamics) and has been obtained by a variety of theoretical methods.

In the case of a degenerate gas (i.e., one for which $e^{-\alpha} = A$ $> > 1$) equation (94) can no longer be used for the evaluation of A, but rather the exact equation (86) from which equation (94) was evolved:

$$N = \Sigma_s \frac{1}{e^{\alpha + \beta \epsilon_s} + 1} \div \frac{2^{5/2} \pi V m^{3/2}}{h^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{\frac{1}{A} e^{\epsilon/k T} + 1} =$$

$$\frac{2^{5/2} \pi V (m k T)^{3/2}}{h^3} \int_0^\infty \frac{u^{1/2} du}{\frac{1}{A} e^u + 1} \quad (100)$$

where u is written for $\frac{\epsilon}{kT}$, and the minus sign corresponding with the assumption of Bose and Einstein is omitted, its significance becoming indefinite for very great values of A. The corresponding integrals for E and pV are:

$$E = \frac{2^{5/2} \pi V k T (m k T)^{3/2}}{h^3} \int_0^\infty \frac{u^{3/2} du}{\frac{1}{A} e^u + 1} \quad (101)$$

$$p V = \frac{2^{5/2} \pi V k T (m k T)^{3/2}}{h^3} \int_0^\infty \log (1 + A e^{-u}) u^{1/2} du \qquad (102)$$

Integration of equation (102) by parts gives:

$$p V = \frac{2}{3} \cdot \frac{2^{5/2} \pi V k T (m k T)^{3/2}}{h^3} \int_0^\infty \frac{u^{3/2} du}{\frac{1}{A} e^u + 1} = \frac{2}{3} E \qquad (103)$$

The generalized integral corresponding with equations (100), (101), etc., is:

$$U_\rho = \frac{1}{\Gamma (\rho + 1)} \int_0^\infty \frac{u^\rho du}{\frac{1}{A} e^u + 1} \qquad (104)$$

where $\rho = 1/2$, $3/2$ etc., and the gamma function of $(\rho + 1)$ dividing the expression serves only in the definition of U_ρ; e.g.,

$$N = \frac{2^{5/2} \pi V (m k T)^{3/2}}{h^3} \cdot U_{\frac{1}{2}} \cdot \Gamma \left(\frac{1}{2} + 1 \right).$$

Sommerfeld has shown that the asymptotic value of U_ρ as $A \to \infty$ (i.e., $A = A_0$) is:

$$\frac{(\log A_0)^{\rho + 1}}{\Gamma (\rho + 2)} \qquad (105)$$

whence, to first approximations, for very large values of A:

$$N = \frac{2^{5/2} \pi V (m k T)^{3/2}}{h^3} \frac{\Gamma (3/2)}{\Gamma (5/2)} (\log A)^{3/2} = \frac{4 \pi V}{3 h^3} (2 m k T)^{3/2} (\log A)^{3/2} \qquad (106)$$

$$E = \frac{2^{5/2} \pi V k T (m k T)^{3/2}}{h^3} \frac{\Gamma (5/2)}{\Gamma (7/2)} (\log A)^{5/2} = \frac{4 \pi V k T}{5 h^3} (2 m k T)^{3/2} (\log A)^{5/2} \qquad (107)$$

Equation (106) gives the value of $\log A$, or more properly $\log A_0$, in terms of measurable quantities:

$$\log A_0 = \left(\frac{3 n}{4 \pi} \right)^{2/3} \frac{h^3}{2 m k T}, \quad \left(n = \frac{N}{V} \right) \qquad (108)$$

Substitution of this value in equation (107) gives for the value of the energy of a highly-degenerate gas:

$$E_0 = \left(\frac{3\,n}{4\,\pi}\right)^{5/3} \frac{2\,\pi\,V\,h^2}{5\,m} \tag{109}$$

Sommerfeld has shown that to a second approximation:

$$\log A = \log A_0 \left[1 - \frac{(2\,\pi\,m\,k\,T)^2}{12\,h^4}\left(\frac{3\,n}{4\,\pi}\right)^{-\frac{4}{3}}\right] \tag{110}$$

and

$$E = E_0 \left[1 + \frac{5}{12}\left(\frac{2\,\pi\,m\,k\,T}{h^2}\right)^2 \left(\frac{3\,n}{4\,\pi}\right)^{-\frac{4}{3}}\right] \tag{111}$$

E_0 is the so-called "Nullpunktsenergie" (independent of T); the corresponding "Nullpunktsdruck" is

$$p_0 = \frac{2}{3}\frac{E_0}{V} = \frac{4\,\pi\,h^2}{15\,m}\left(\frac{3\,n}{4\,\pi}\right)^{5/3} \tag{112}$$

The "Nullpunktsentropie" is directly obtained from equation (89):

$$S_0 = N\,k\,\alpha_0 + k\,\beta\,E_0 + k\,\sum_s \log\left(1 + e^{-\alpha_0 - \beta\,\epsilon_s}\right)$$

$$\left[\alpha_0 = -\log A_0;\ \beta = \frac{1}{k\,T};\ k\,\sum_s \log\left(1 + e^{-\alpha_0 - \beta\,\epsilon_s}\right) = \frac{p_0\,V}{T} = \frac{2}{3}\frac{E_0}{T}\right]$$

whence

$$N\,k\left[-\log A_0 + \frac{5}{3}\frac{E_0}{N\,k\,T}\right] \tag{113}$$

From equations (100), (101), (104), (105),

$$\frac{5}{3}\frac{E_0}{N\,k\,T} = \frac{5}{3}\frac{\Gamma\,(5/2)}{\Gamma\,(3/2)}\frac{U_{3/2}}{U_{1/2}} = \frac{5}{3}\frac{\Gamma\,(5/2)}{\Gamma\,(3/2)}\frac{\Gamma\,(5/2)}{\Gamma\,(7/2)}\frac{(\log A_0)^{5/2}}{(\log A_0)^{3/2}} = \log A_0$$

$$[\Gamma (1/2) = \sqrt{\pi}; \ \Gamma (x + 1) = x \ \Gamma (x), \text{ if } x > 0]$$

$$S_0 = 0$$

In the development of the statistics of (rotationless) mona-
tomic gases just given, the statistical weight (or a priori probability)
of each infinitesimal region of the phase-space is postulated to be
equal to the extension in phase-space divided by the constant h^3,
i.e.,

$$\frac{dp_x \ dp_y \ dp_z \ dx \ dy \ dz}{h^3}$$

This corresponds with the assignment of a statistical weight equal
to unity for each mechanically possible stationary state of a
("non-degenerate") quantized system.

Current theories regarding the electron assign to it a spin.
This consideration requires that its statistical weight be twice
that of a rotationless mass-point, i.e.,

$$\frac{G}{h^3} \ dp_x \ dp_y \ dp_z \ dx \ dy \ dz, \ (G = 2)$$

Thus, in the application of the preceding formulas to electrons, in
every instance $\frac{1}{h}$ is replaced by $\frac{G^{\frac{1}{3}}}{h}$. The following list of
altered and extended formulas is given for convenience in the
subsequent deductions.[1]

$$\frac{N}{V} = \frac{2^{5/2} \ \pi \ G \ (m \ k \ T)^{3/2}}{h^3} \int_0^\infty f_0 \ u^{1/2} \ du; \ \left(f_0 = \frac{1}{\frac{1}{A} e^u + 1} \right) \tag{114}$$

$$U_\rho = \frac{1}{\Gamma \ (\rho + 1)} \int_0^\infty f_0 \ u^\rho \ du \tag{115}$$

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[1] In the case of a non-degenerate gas, it is evident that $f_0 = \dfrac{1}{\dfrac{1}{A} e^u + 1}$ becomes
essentially $A \ e^{-u}$, as in the Lorentz application of the classical statistics. See
Sommerfeld's derivation of the Lorentz formulas, Z. Physik 47, 23, 26 (1928).

To a second approximation:

$$U_0 = \log A \tag{116}$$

$$U_1 = \frac{(\log A)^2}{2\,!}\left[1 + \frac{\pi^2}{3\,(\log A)^2}\right] \tag{117}$$

$$U_2 = \frac{(\log A)^3}{3\,!}\left[1 + \frac{\pi^2}{(\log A)^2}\right] \tag{118}$$

$$\log A = \frac{h^2}{2\,m\,k\,T}\left(\frac{3\,n}{4\,\pi\,G}\right)^{2/3}\left[1 - \frac{1}{12}\left(\frac{2\,\pi\,m\,k\,T}{h^2}\right)^2\left(\frac{3\,n}{4\,\pi\,G}\right)^{-\frac{4}{3}}\right] \tag{119}$$

From equation (111), with the proper insertion of G,

$$E = \frac{2\,\pi}{5}\frac{V\,G\,h^2}{m}\left(\frac{3\,n}{4\,\pi\,G}\right)^{5/3}\left[1 + \frac{5}{12}\frac{(2\,\pi\,m\,k\,T)^2}{h^4}\left(\frac{3\,n}{4\,\pi\,G}\right)^{-\frac{4}{3}}\right] \tag{120}$$

Whence the heat capacity of the electron-gas is

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \frac{4\,\pi^2\,m\,G\,V\,k^2\,T}{3\,h^2}\left(\frac{3\,n}{4\,\pi\,G}\right)^{1/3} \tag{121}$$

a quantity which is negligibly small for metals at ordinary temperatures.

With the Fermi distribution function [f_0 of equation (114)], equations (21) and (21a) for the electric current per unit cross-section and the quantity of heat transported per second per unit cross-section, become respectively:

$$J = -\,e\,l\int\frac{\xi}{v}\left(X\frac{\partial f_0}{\partial \xi} + \xi\frac{\partial f_0}{\partial x}\right)d\Omega \tag{122}$$

$$W = -\,\frac{m\,l}{2}\int\xi\,v\left(X\frac{\partial f_0}{\partial \xi} + \xi\frac{\partial f_0}{\partial x}\right)d\Omega \tag{122a}$$

where

$$d\Omega = 4\,\pi\,G\left(\frac{m}{h}\right)^3 v^2\,dv = B\,v^2\,dv \tag{123}$$

$$\frac{1}{\xi}\frac{\partial f_0}{\partial \xi} = \frac{1}{v}\frac{\partial f_0}{\partial v}; \quad [v^2 = \xi^2 + \eta^2 + \zeta^2]; \quad \xi^2 = \frac{1}{3}v^2$$

Whence

$$J = -\frac{e\,l\,B}{3}\left\{X\int\frac{\partial f_0}{\partial v}v^3\,dv + \frac{\partial}{\partial x}\int v^3 f_0\,dv\right\} \tag{124}$$

$$W = -\frac{m\,l\,B}{6}\left\{X\int\frac{\partial f_0}{\partial v}v^4\,dv + \frac{\partial}{\partial x}\int v^5 f_0\,dv\right\} \tag{124a}$$

By a change of variable, $u = \dfrac{m\,v^2}{2\,k\,T}$, the equations become:

$$J = -\frac{e\,l\,B}{-}\left|2\,k\,T\,X\int u\frac{\partial f_0}{\partial u}\,du + \frac{\partial}{\partial x}\left[2\left(\frac{k\,T}{m}\right)^2\int f_0\,u\,du\right]\right\} \tag{125}$$

$$W = -\frac{m\,l\,B}{6}\left\{\left(\frac{2\,k\,T}{m}\right)^2 X\int u^2\frac{\partial f_0}{\partial u}\,du + \frac{\partial}{\partial x}\left[4\left(\frac{k\,T}{m}\right)^3\int f_0\,u^2\,du\right]\right\} \tag{125a}$$

Integration by parts of the first terms on the right gives:

$$J = \frac{e\,l\,B}{-}\left|2\,k\,T\,X\int f_0\,du - \frac{\partial}{\partial x}\left[2\left(\frac{k\,T}{m}\right)^2\int f_0\,u\,du\right]\right\} \tag{126}$$

$$W = \frac{m\,l\,B}{6}\left\{8\left(\frac{k\,T}{m}\right)^2 X\int f_0\,u\,du - \frac{\partial}{\partial x}\left[4\left(\frac{k\,T}{m}\right)^3\int f_0\,u^2\,du\right]\right\} \tag{126a}$$

These integrals correspond with the generalized integral of equation (115) with ρ having the values 0, 1, 2.

Whence

$$J = \frac{2\,e\,l\,B}{3}\left\{\frac{k\,T\,X}{m}U_0 - \frac{\partial}{\partial x}\left[\left(\frac{k\,T}{m}\right)^2 U_1\right]\right\} \tag{127}$$

$$W = \frac{4\,m\,l\,B}{3}\left\{\left(\frac{k\,T}{m}\right)^2 X\,U_1 - \frac{\partial}{\partial x}\left[\left(\frac{k\,T}{m}\right)^3 U_2\right]\right\} \tag{127a}$$

For the case of electrical conductivity in a conductor at constant temperature,

$$\left[\frac{\partial T}{\partial x} = 0, \ \frac{\partial U_1}{\partial x} = \frac{\partial U_1}{\partial T} \frac{\partial T}{\partial x} = 0 \right]$$

and with the acceleration X given by $\dfrac{e\,E}{m}$, where E is the electric intensity, it follows that the coefficient of electrical conductivity is:

$$\sigma \quad \frac{J}{E} \quad \frac{2}{3} \quad \frac{e^2\, l\, k\, T}{m^2} \ B\, U_0 \tag{128}$$

Substitution from equations (123), (116), and (119), the first approximation for $\log A$ being used, $(G = 2)$, gives:

$$\sigma = \frac{8\,\pi}{3} \frac{e^2\, l}{h} \left(\frac{3\,n}{8\,\pi} \right)^{2/3} \tag{129}$$

In the case of a thermal conductor in which there is no electrical current:

$$J = 0 \quad \frac{2\,e\,l\,B}{3} \left| \frac{k\,T\,X\,U_0}{m} - \frac{\partial}{\partial x} \left[\left(\frac{k\,T}{m} \right)^2 U_1 \right] \right\} \tag{130}$$

and

$$\triangle - \frac{m}{k\,T\,U_0} \frac{\partial}{\partial x} \left[\left(\frac{k\,T}{m} \right)^2 U_1 \right] \tag{131}$$

Whence, by substitution in (127a):

$$W = \frac{4\,l\,B}{3\,m^2} \left\{ k\,T\, \frac{U_1}{U_0} \frac{\partial}{\partial x} \left[(k\,T)^2\, U_1 \right] - \frac{\partial}{\partial x} \left[(k\,T)^3\, U_2 \right] \right\} \tag{132}$$

$$= \frac{4\,l\,B}{3\,m^2} \left[(k\,T)^3 \frac{U_1}{U_0} \frac{\partial\,U_1}{\partial x} + 2\, \frac{k^3\,T^2\,U_1^2}{U_0} \frac{\partial\,T}{\partial x} - (k\,T)^3 \frac{\partial\,U_2}{\partial x} - 3\,k^3\,T^2\,U_2 \frac{\partial\,T}{\partial x} \right]$$

From equations (117) and (118)

$$\frac{U_1}{U_0} \frac{\partial\,U_1}{\partial x} = \frac{\partial\,U_2}{\partial x} \tag{133}$$

Whence,

$$W = \frac{4\, l\, B\, k^3\, T^2\, U_1}{3\, m^2} \left(2\, \frac{U_1}{U_0} - 3\, \frac{U_2}{U_1} \right) \frac{\partial T}{\partial x} \qquad (134)$$

Substitutions corresponding with equation (123) for B and with (119), (120) for U_1 and U_2, give for the coefficient of thermal conductivity:

$$\kappa = -\frac{W}{\dfrac{\partial T}{\partial x}} = \frac{8}{9}\, \frac{\pi^2\, l\, k^2\, T}{h} \left(\frac{3\, n}{8\, \pi} \right)^{2/3} \qquad (135)$$

From equations (129) and (135), it follows that the Wiedemann-Franz ratio $\frac{\kappa}{\sigma}$, according to the Fermi statistics, has the value $\frac{\pi^2}{3}\left(\frac{k}{e}\right)^2 T$, or 7.1×10^{-11} for a temperature of 291°K. This value is in remarkably close agreement with the mean value of the ratio for the twelve common metals Al, Ag, Au, Cd, Cu, Fe, Ni, Pb, Pt, Sn, Zn; the individual experimental values however depart appreciably from this mean value.

In spite of the closely agreeing value for the Wiedemann-Franz ratio, a glance at formula (129) for the coefficient of electrical conductivity reveals the fact that it does not give the proper temperature coefficient of the conductivity,—at least if l is assumed independent of the temperature (i.e., independent of the average velocity, $\bar{v}$). Sommerfeld has shown that the same formulas (129) (135) are obtained if, throughout the calculation, l is considered as a function of the velocity. According to the wave-theory of electrons, developed by Houston and Bloch, the quantity l is a function of temperature, the atoms of the metal becoming more effective in electron-scattering the higher the temperature. Houston has shown theoretically by this method of reasoning that the conductivity of a perfect crystal varies inversely as the temperature over a considerable range of temperature.

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THE REACTIONS OF HALOGENS WITH COMPOUNDS CONTAINING THE CARBONYL GROUP

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I. KETONES AND KETONIC ACIDS

It was first suggested by Lapworth (53) in 1904 that the characteristic replacement by halogens of the α-hydrogen atom in carbonyl compounds might involve a preliminary change of the compound to its enolic form,

$$\overset{|}{\underset{|}{C}}=O \rightarrow =\overset{|}{C}-OH.$$
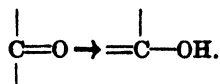
The suggestion was based on his discovery that bromine reacts with acetone in dilute aqueous solution (to give monobromoacetone) at a rate which is proportional to the concentration of the ketone, but independent of that of the halogen; the reaction, moreover, is accelerated to a very marked extent by mineral acids (well-known catalysts of keto-enol changes (52) (54) (62)). These observations led Lapworth to suggest that a slow change to the enolic form (catalyzed by acids) is followed by a very rapid reaction of the latter with bromine,

$$CH_3 \cdot CO \cdot CH_3 \xrightarrow{\text{(slow)}} CH_2 : C(OH) \cdot CH_3 \xrightarrow{\text{Br}_2 \text{ (rapid)}} CH_2Br \cdot CO \cdot CH_3 + HBr.$$
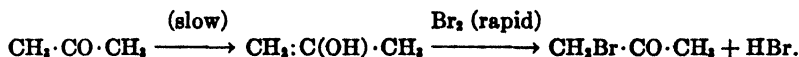
The results of Dawson and his co-workers (14, 15, 16, 17, 18), who examined the iodination of acetone and other ketones and of acetaldehyde, confirmed the conclusion that the reactions of the halogens with ketones and aldehydes are preceded by enolization of the carbonyl compound.

An extensive investigation of the keto-enol tautomerism of the β-diketones and β-ketonic esters (e.g. acetylacetone, ethyl acetoacetate) by K. H. Meyer, Knorr, and others, showed that

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these substances exhibit this type of isomerism with great clearness. In the case of acetone, the actual existence of an enolide has never been demonstrated, although Freer (24, 25, 26, 27, 28, 29) has attributed an enolic structure to certain metallic derivatives, and the presence of enolide in alkaline solutions has been inferred (20) (23) (100) from the nature of its oxidation products. The β-diketones and β-ketonic esters, on the other hand, are normally equilibrium mixtures of the ketonic and enolic forms, and the relative amounts of each present have been determined by both physical and chemical methods. Moreover, in a number of instances, the individual tautomerides have been isolated in the pure state (50) (51) (65), e.g., the two forms $CH_3 \cdot CO \cdot CH_2 \cdot COOEt$ and $CH_3 \cdot C(OH):CH \cdot COOEt$ of ethyl acetoacetate. Bromine reacts instantaneously with the enolides, but not with the ketonic isomers.

It has recently been demonstrated, particularly by Dufraisse and H. Moureu (21) (22) (67) (68), that the α-diketones also are tautomeric substances, and these workers have isolated the individual isomerides of phenylbenzyl, phenylanisyl, and benzylmethyl diketones. The existence of the same phenomenon in the α-ketonic acids was indicated by the work of Schiff (84), Bougault and Hemmerlé (6), and Gault and Weick (31), the last-named of whom isolated three forms of ethyl phenylpyruvate (the ketonic and two stereoisomeric monoenolic forms). Further evidence of the enolization of α-ketonic acids has recently been obtained (42) by an investigation of the kinetics of bromination of pyruvic acid. In aqueous solution, the acid reacts with bromine at a rate which is independent of the concentration of the halogen, and this result is interpreted in a simple manner (compare acetone) by supposing that a comparatively slow change to enolide is followed by a rapid reaction of the latter with bromine,

$$CH_3 \cdot CO \cdot COOH \xrightarrow{\text{(slow)}} CH_3:C(OH) \cdot COOH \xrightarrow{\text{Br}_2 \text{ (rapid)}} CH_2Br \cdot CO \cdot COOH + HBr.$$

The pure acid, however, under ordinary conditions, contains no appreciable amount of enolide, since the measurable reaction is never preceded by an instantaneous disappearance of a portion

of the bromine. This is in harmony with the results of the physical measurements of Perkin (76) and Brühl (9).

Although keto-enol tautomerism is clearly possible also in γ-diketones and γ-ketonic acids, its existence has not been demonstrated until recently. Investigation of the bromination of levulic acid in aqueous solution (42) has now indicated, however, that this acid reacts with bromine in its enolic form to give the β-brominated derivative,

$$\text{(slow)}$$
$$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH \longrightarrow CH_3 \cdot C(OH) : CH \cdot CH_2 \cdot COOH$$

$$Br_2 \text{ (rapid)}$$
$$\longrightarrow CH_3 \cdot CO \cdot CHBr \cdot CH_2 \cdot COOH + HBr,$$
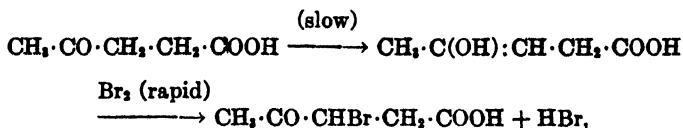
while the latter reacts more slowly, also after enolization, to form βδ-dibromolevulic acid,

$$\text{(slow)}$$
$$CH_3 \cdot CO \cdot CHBr \cdot CH_2 \cdot COOH \longrightarrow CH_2 : C(OH) \cdot CHBr \cdot CH_2 \cdot COOH$$

$$Br_2 \text{ (rapid)}$$
$$\longrightarrow CH_2Br \cdot CO \cdot CHBr \cdot CH_2 \cdot COOH + HBr.$$
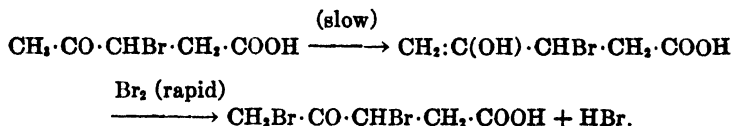
The facts outlined above point to the conclusion that, in general, the reactions of halogens with ketones, aldehydes, diketones, and ketonic acids are preceded by a change of the carbonyl compound to its enolic form. It is significant, however, that the enolide $CH_3 \cdot CO \cdot CH : C(OH)_2$ of ethyl acetoacetate has never been observed, while levulic acid brominates in the β- and δ-positions and not in the α-position. Such evidence appears to indicate that, in the carboxyl group, the properties are modified in such a way that enolization does not occur. This is discussed fully in section II of this paper.

The mechanism of enolization and other prototropic changes has recently been discussed in terms of the electronic theory of valency, by Lowry (57) (58), Ingold, Shoppee and Thorpe (46), and Baker (3). Lowry believes (and the suggestion dates back as far as 1899) that prototropic changes are not spontaneous, but depend upon the presence in the system of other molecules; this idea is based upon the observation of arrests of irregular duration

in the mutarotation of nitrocamphor (56) and of tetramethyl-glucose (61) in anhydrous media. He defines such arrests as the "period of time during which a pure substance is taking up the impurities which are needed to promote the change." Experiments on the bromination of acetone, pyruvic acid and levulic acid (42) in chloroform or carbon tetrachloride medium confirm Lowry's view. In aqueous solution these substances react with bromine at a slow rate, i.e., slow enolization takes place, but in the anhydrous solvents there is a relatively rapid reaction after an initial latent period, the duration of which varies for different portions of the same specimens of the reagents. Ward (92) observed a similar phenomenon in the bromination of pure pyruvic acid. The experimental facts point, therefore, to the conclusion that enolization takes place only when some outside agent is introduced or developed in the system.

According to Lowry, prototropic changes are possible only in presence of both a proton donator and a proton acceptor, the change consisting not merely in the transference of a proton from one point in the molecule to another, but in the release of the proton to the acceptor and the gain of another proton from the donator. This theory, as applied to mutarotation, has been verified in a striking manner by the observation (60) that, although pyridine (proton acceptor) and cresol (proton donator) do not individually catalyze the mutarotation of tetramethylglucose, the two acting in conjunction form a powerful catalyst. Lowry's view, therefore, is that two catalytic agents are necessary for the promotion of prototropic changes; he describes water, however, as a "complete catalyst," since it fulfils both functions. As an extension of these ideas, Lowry has elaborated (58) a mechanism to represent the change of enolide to ketone, which, when applied to the reverse change, may be formulated as follows:

According to this scheme, the catalyst has no function other than that of proton acceptor and donator. A somewhat different view of the effects of catalysts on prototropic changes has been put forward by Baker (3); on the basis of a mechanism suggested by Ingold, Shoppee and Thorpe (46) to represent the interconversion of three-carbon tautomerides, he suggests that catalysts are of two types,—(a) those whch attack the ionizing proton directly, and (b) those which facilitate indirectly its liberation.

It was pointed out by Meyer (62) that acids catalyze enolization far more powerfully in non-ionizing than in ionizing media—i.e., the acid exerts a far greater influence when in the covalent state (vide Sidgwick, Electronic Theory of Valency, p. 93) than when ionized. This fact has been further demonstrated by the author's measurements of the speeds of halogenation of carbonyl compounds in different media, and particularly by the observation that, in moist chloroform, the bromination of acetone, pyruvic acid and levulic acid (autocatalyzed by hydrogen bromide), although not showing an arrest, is very much slower than in dry chloroform. It is difficult to understand how this could be the case if the function of the catalyst is only that of proton donator and acceptor, but the observed effects of water and acids upon enolization may perhaps be interpreted by the following scheme, which includes the ideas of both Lowry and Baker. Water is regarded as merely giving and accepting a proton, while acids combine these functions with that of facilitating the removal of the proton (Baker's second type).

In carbonyl compounds there is doubtless a partial appropriation of electrons by the oxygen atom of the carbonyl group (81) (5), and in the general case of a compound $CH_3 \cdot CO \cdot Z$ (where $Z = CH_3$, COOH, etc.) this will result in one of the hydrogen atoms of the methyl group being in a state of "incipient ionization" (41) (46),
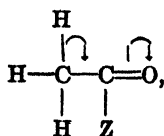
i.e., the electrons forming the covalent link are not shared equally, but come more under the influence of the carbon than of the hydrogen nucleus. Considering now the case of enolization, (a) in pure water, (b) in water in presence of halogen or other acid, and (c) in non-ionizing media in presence of acids, the agents by which the change is induced are respectively, (a) H_2O, (b) the H_3O^+ ion, (c) the covalent acid. These may be regarded as coördinating with the carbonyl oxygen, to give respectively,
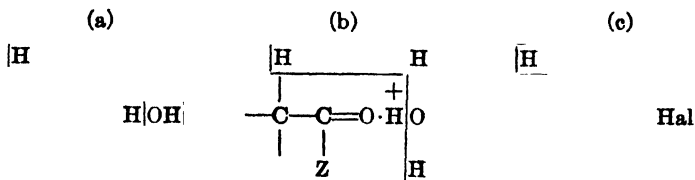
The coördinated group thus provides a proton. In cases (b) and (c), however, an additional influence comes into play, for the "inductive effect" (44) of the positive pole in (b) and of the halogen atom in (c) will augment the electron shifts which lead to the ionizing of the proton, and will thus facilitate enolization.[1] The remainder of the coördinated group (OH', H_2O, Hal') will then withdraw the incipiently ionized hydrogen atom, and these processes, together with the consequent movement of electrons through the molecule (perhaps as indicated by Lowry), will result in the production of the enolide.

On this scheme, water acts only (as in Lowry's mechanism) as a proton acceptor and donator, but acids, both ionized and covalent, also accelerate the change by rendering more easy the ionizing of the proton. The catalytic effect of acids is thus interpreted. Moreover, the superiority of covalent to ionized acids as catalysts is explained, for the proton will clearly unite with a bromine (or other negative) ion to give covalent acid more readily than with a neutral water molecule to give the H_3O^+ ion.

[1] The powerful electron affinity of the halogens is exemplified in the increasing proportion of meta-derivative formed in the nitration of the series toluene, benzyl chloride, benzal chloride, benzotrichloride; $PhCH_3$, 4.4%; $PhCH_2Cl$, 16%; $PhCHCl_2$, 33.8%; $PhCCl_3$, 64.5%. Holleman; Rec. trav. chim. **33**, 1 (1914). Baker and Ingold: J. Chem. Soc. **1926**, 2466. Ingold and Rothstein: ibid. **1928**, 1278.

Considering now the special case of ketonic acids, and taking pyruvic, acetoacetic and levulic acids as typical examples of the α-, β-, and γ-types, the effect of the partial appropriation of electrons by the carbonyl oxygen may be represented as follows (oxygen in the *carboxyl* group does not have this effect, see following section);
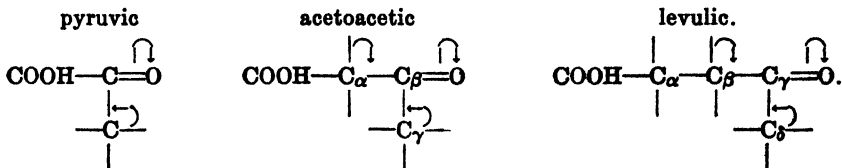
In acetoacetic and levulic acids, therefore, the effect is shared by an α- and a γ-hydrogen atom and by a β- and a δ-hydrogen atom respectively. Superimposed on this, however, is the inductive effect of the carboxyl group,[2] and as early as 1904 the different enolizing tendencies of acetone and ethyl acetoacetate were ascribed by Lowry to the presence of the carbethoxyl group in the latter. This effect of the carboxyl group causes pyruvic acid to enolize more rapidly than acetone; moreover, it tends powerfully towards the ionization of the α-hydrogen of acetoacetic acid, and the β-hydrogen of levulic acid. This is in harmony with the facts that (a) in ethyl acetoacetate only the *one* enolide $CH_3 \cdot C(OH):CH \cdot COOH$ is known, and (b) the β-hydrogen atom of levulic acid enolizes more readily than the δ-hydrogen atom. The tendency to enolization is undoubtedly stronger in acetoacetic than in levulic acid (ethyl acetoacetate normally contains 7 per cent of enol), and this may be attributed to a screening of the effect of the carboxyl group in the latter by the α-carbon atom.[3]

There is, therefore, a large amount of experimental evidence for the assertion that, in general, compounds containing a car-

[2] Attraction of electrons, as indicated, for example, by the fact that nitration of benzoic acid yields 80.2 per cent of the meta-derivative. Holleman: Rec. trav. chim. **18**, 267 (1899). Ingold: Annual Report **1926**, 138.

[3] Compare the decrease in percentage of meta-derivative in the nitration of the series nitrobenzene, phenylnitromethane, β-phenyl-nitroethane: $PhNO_2$, 93%; $PhCH_2NO_2$, 48%; $PhCH_2CH_2NO_2$, 13%. Ingold: Annual Report **1926**, 132.

bonyl group (excluding the *carboxyl* group), with at least one hydrogen atom situated in the α-position with respect to that group, react with halogens in their enolic forms. Moreover, the phenomena observed are such as would be anticipated, on theoretical grounds, from the electronic theory of valency.

II. CARBOXYLIC ACIDS

The case of the carboxyl group calls for special discussion, and is best illustrated by reference to acetic acid and its homologues. At the ordinary temperature these acids are not attacked by chlorine or bromine at an appreciable rate, but at a more elevated temperature (e.g., 100°) replacement of one α-hydrogen occurs,

$$R \cdot CH_2 \cdot COOH + X_2 = R \cdot CHX \cdot COOH + HX$$

The replacement of a second α-hydrogen atom is a matter of very considerable difficulty, and if there is no α-hydrogen atom, substitution does not take place, as is exemplified by the fact that trimethylacetic acid gives no brominated acid when treated with bromine at 100–135° (82).

The facts that substitution always takes place at the α-position, and that the reaction is accelerated by halogen acids (first observed by Hell and Mühlhäuser (36)) appear to indicate an analogy with the bromination of acetone, and Lapworth (53) in 1904 suggested tentatively that the acid might perhaps react in its enolic form, according to the scheme

$$R \cdot CH_2 \cdot COOH \xrightarrow{\text{(slow)}} R \cdot CH:C(OH)_2 \xrightarrow{\text{Br}_2 \text{ (rapid)}} R \cdot CHBr \cdot COOH + HBr.$$
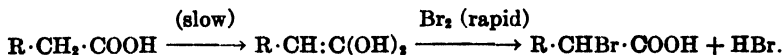
The catalytic influence of halogen acids would then consist in an acceleration of the enolization. Aschan (1) adopted Lapworth's suggestion to explain the production of brominated acid bromide, as well as brominated acid chloride, when bromine reacts with an acid chloride, which he represented
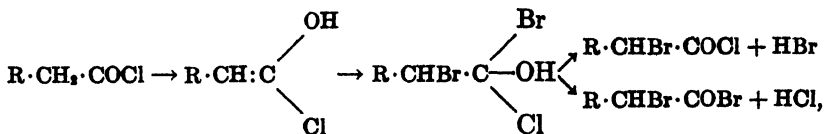
but Meyer pointed out (64) that such an interpretation is unnecessary, since the observation is explained equally well by postulating bromination of the ketonic form, followed by a reaction of hydrogen bromide with the brominated acid chloride,

$$R \cdot CHBr \cdot COCl + HBr \rightleftarrows R \cdot CHBr \cdot COBr + HCl,$$
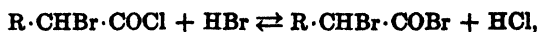
a type of reaction which is known to occur under suitable conditions (87) (66).

It is curious that the supporters of the "enolic form theory" apparently overlooked the results of Hell and Urech (37), who observed that the rate of bromination of acetic acid and its homologues is dependent upon the concentration of bromine; this could not be the case if slow enolization were followed by a practically instantaneous reaction of the enolide with halogen. The theory, moreover, demands the existence of the carboxylic acid in a form which is neither observed nor indicated elsewhere. It may also be urged that, since the reactions of the carbonyl group of a carboxylic acid differ in many respects from those of the same group in a ketone, it is unsafe to force an analogy between the two types of compounds, and the distinction is borne out by the fact that many physical properties of carboxylic acids (e.g., refractive index, Brühl (10); diamagnetism, Pascal (75); rotatory dispersion, Pickard and Kenyon (78); optical absorption, Hantzsch (35); parachor, Sugden (88)) do not give the values which would be anticipated if a carbonyl group of the usual type were present.   In the light of these facts, a number of investiga-

tors have supposed that the ordinarily accepted formula $R. C \overset{\displaystyle O}{\underset{\displaystyle OH}{\diagup\!\!\!\diagup}}$

is not a correct representation, and alternative formulas such as
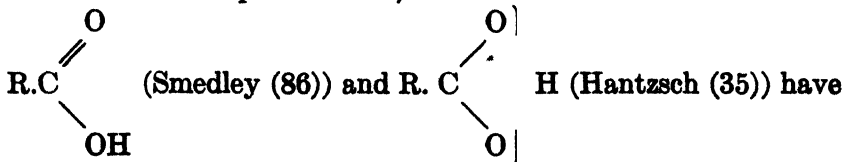
$R.C \overset{\displaystyle O}{\underset{\displaystyle OH}{\diagup\!\!\!\diagup}}$ (Smedley (86)) and $R. C \overset{\displaystyle O\rceil}{\underset{\displaystyle O\rfloor}{\diagup\cdot}} H$ (Hantzsch (35)) have

been suggested.   On modern views, the failure of the carboxyl

group to exhibit the typical carbonyl reactions is ascribed to the competition $\overset{\frown}{HO} - C = \overset{\frown}{O}$ (81) (46); the effect of the partial appropriation of electrons by the carbonyl oxygen is thus neutralized, and the tendency of the α-hydrogen atom to ionize is removed. It is not to be expected, therefore, that the halogenation of acetic acid and its homologues will be preceded by a change of the acid to its enolic form, and this has been demonstrated by an investigation of the kinetics of these reactions at 100° (93) (95) (97) (96).

The investigation has provided definite confirmation of the facts (first stated by Hell and Urech (37)) that the speed of bromination of these acids is (a) dependent upon the concentration of bromine, and (b) increased by the presence of halogen acids.

TABLE 1

Bromination of acetic acid at 100°C.

Catalyst added.....	nil	HBr = 0.053M	HCl = 0.064M	AcBr = 0.047M
Initial titre	9.48	9.58	10.02	9.55
Fall in 30 minutes..	0.20	1.05	0.52	8.00

Thus, when no catalyst is present initally, the course of the reaction indicates autocatalysis by the hydrogen bromide produced, for the rate of disappearance of bromine gradually rises to a maximum and finally decreases; variation in the initial concentration of bromine has a marked effect, while the presence of a moderate initial concentration of hydrogen bromide induces a much faster reaction, the period of increasing speed disappearing. The effect of hydrogen chloride resembles that of hydrogen bromide, but is somewhat less powerful. The influence of halogen acids, however, is specific, and not common to acids in general, for sulfuric and trichloroacetic acids do not have a similar effect; the acceleration produced by halogen acids is not likely, therefore, to consist merely in a speeding up of the enolization of the carboxylic acid, and this fact, together with the dependence of the velocity upon the concentration of bromine, provides evidence against the validity of the simple "enolic form theory."

The outstanding feature of the reaction, as revealed in this

investigation, is the enormous acceleration produced by a small quantity of an acid bromide, different acid bromides having identical effects. The magnitude of this acceleration is obvious from table 1. Further, in presence of acetyl bromide (or other acid bromide), the velocity is proportional to the concentration of both acid bromide and bromine. The autocatalytic effect of the hydrogen bromide formed during the reaction will clearly be inappreciable in the presence of the more powerful accelerator.

A similar rapid reaction results from the introduction of an acid anhydride (compare Hentschel (38); Shaw (85)) or acid chloride, but there is now an initial period of relatively low but increasing speed; this period is easily interpreted as the time needed for the conversion of anhydride or acid chloride into acid bromide,

$$(R \cdot CH_2 \cdot CO)_2O + Br_2 = R \cdot CHBr \cdot COOH + R \cdot CH_2 \cdot COBr$$
$$(R \cdot CH_2 \cdot CO)_2O + HBr \rightleftarrows R \cdot CH_2 \cdot COOH + R \cdot CH_2 \cdot COBr$$
$$R \cdot CH_2 \cdot COCl + HBr \rightleftarrows R \cdot CH_2 \cdot COBr + HCl,$$
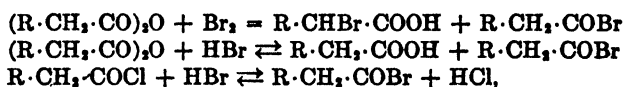
and such an explanation is confirmed by two observations: (a) the initial period disappears if excess of hydrogen bromide is introduced with the anhydride; the latter is doubtless, under these conditions, converted very rapidly to acid bromide (this reaction proceeds readily even at room temperature), and the bromide is thus present from the commencement at its maximum concentration; (b) excess of hydrogen chloride introduced in conjunction with the anhydride has a retarding influence; the anhydride now forms acid chloride,

$$(R \cdot CH_2 \cdot CO)_2O + HCl \rightleftarrows R \cdot CH_2 \cdot COOH + R \cdot CH_2 \cdot COCl$$
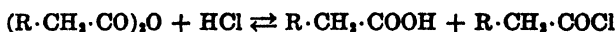
(Gal (30)), and anything approaching complete conversion to acid bromide during the reaction is prevented by the excess of hydrogen chloride.

Investigation of the chlorination of acetic acid has yielded a similar series of observations (the acid chloride here being the powerful accelerator), except that (a) the reaction is somewhat slower than bromination, and (b) in presence of an acid chloride the velocity decreases less rapidly than the concentration of chlorine. These peculiarities are discussed later (p. 185).

An interpretation of the facts outlined above may be found in the following considerations. It has long been known that halogens react with the halides of carboxylic acids more rapidly than with the acids themselves, and the Hell-Volhard method of bromination is based upon this fact. The peculiarly powerful effect of acyl halides as accelerators of the halogenation of carboxylic acids may be interpreted, accordingly, by supposing that the halide first reacts with halogen,

$$R \cdot CH_2 \cdot COX + X_2 = R \cdot CHX \cdot COX + HX, \tag{1}$$

the halogenated acid then being formed as the result of a reaction between the unsubstituted acid and the halogenated halide,

$$R \cdot CHX \cdot COX + R \cdot CH_2 \cdot COOH \rightleftarrows R \cdot CH_2 \cdot COX + R \cdot CHX \cdot COOH. \tag{2}$$

The acyl halide is thus free to go through the same series of changes again. If the halide of a different carboxylic acid be present initially, reactions (1) and (2) will be preceded by

$$R' \cdot COX + R \cdot CH_2 \cdot COOH \rightleftarrows R \cdot CH_2 \cdot COX + R' \cdot COOH, \tag{2a}$$
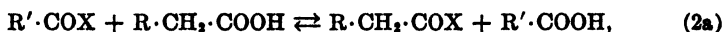
which is exactly similar in character to reaction (2).

It has been suggested by Hentschel (38), Shaw (85) and Brückner (8) that the halogenation of carboxylic acids proceeds through the anhydride (which also reacts with halogens far more readily than does the acid itself), by the following pair of alternating reactions,

$$(R \cdot CH_2 \cdot CO)_2O + X_2 = R \cdot CH_2 \cdot COX + R \cdot CHX \cdot COOH$$
$$R \cdot CH_2 \cdot COX + R \cdot CH_2 \cdot COOH \rightleftarrows (R \cdot CH_2 \cdot CO)_2O + HX.$$

It has been pointed out above, however, that in both chlorination and bromination the introduction of a small amount of the acid anhydride leads to a rapid reaction *after* an initial period of relatively low speed, while there is no such period when the appropriate acid halide is introduced; this observation indicates clearly that the halogenation proceeds through the halide, the initial period being easily accounted for as described above.

It will be seen from the following discussion of other relevant facts that the author's scheme is supported by a considerable amount of experimental evidence.

Reaction (*1*) (p. 184). The results of Urech (90) indicate that the bromination of acetyl bromide proceeds at a rate which is proportional to the concentrations of bromine and of acid bromide, and the author has confirmed this observation by an investigation of the reaction at 25° (95), using an apparatus specially designed to avoid contact of the acid bromide with atmospheric moisture. If now, in the scheme outlined above, reaction (2) proceeds at very great speed, and practically to completion in presence of the excess of the carboxylic acid (as is indicated in the case of the analogous reaction (2a) by the identical effects of different acid bromides), the concentration of acyl halide will remain constant during any given reaction, and the velocity will vary, therefore, only as the concentration of bromine, but will be proportional to the initial concentration of the acyl bromide. This is in complete agreement with the observed facts for the bromination of carboxylic acids, and it is clear, therefore, that the halogen does not react with the enolic form of the acid to a measurable degree, a conclusion which is confirmed by the observation that such powerful accelerators of enolization as sulfuric acid and ferric chloride do not affect the halogenation appreciably.

In the case of chlorination (97), complications arise from the fact that side reactions take place during the chlorination of acetyl chloride. The velocity of chlorination of the pure chloride, in fact, actually increases as the reaction proceeds, owing to these side reactions (which however are imperceptible in presence of a powerful catalyst such as iodine, when the velocity is proportional to the concentration of chlorine), and it is thus easy to explain the absence, in the chlorination of acetic acid, of a simple relation between the fall in concentration of chlorine and the velocity.

It appears at first sight remarkable that chlorination is slower than bromination. This is due, however, to the fact that halogens react with acid chlorides far less rapidly than with acid bromides; for example, the reactions (*a*) acetyl bromide + bromine, (*b*) acetyl chloride + bromine, (*c*) acetyl chloride + chlorine, stand in decreasing order of speed. In view of this fact, the chlorination of acetic acid, which involves the reaction of

chlorine with acetyl chloride, must be less rapid than its bromination, which depends upon the reaction of bromine with acetyl bromide. Moreover, in presence of an acid chloride, the bromination of acetic acid doubtless proceeds through the series of reactions:

$$CH_3 \cdot COCl + Br_2 = CH_2Br \cdot COCl + HBr$$
$$CH_2Br \cdot COCl + CH_3 \cdot COOH \rightleftharpoons CH_2Br \cdot COOH + CH_3 \cdot COCl.$$
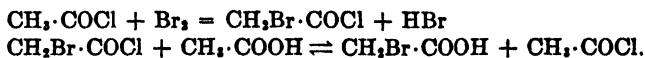
The reaction is not rapid, however, owing to the relatively slow rate of bromination of acetyl chloride. Hence, the reaction of bromine with a carboxylic acid in presence of an acid chloride does not reach its maximum speed until sufficient hydrogen bromide has been formed to bring about conversion of acid chloride to acid bromide; the above reactions are then replaced by those in which the acid bromide takes part.

Finally, the relative rates of halogenation of the compounds considered above are such as would be predicted on theoretical grounds. It has already been pointed out (p. 182) that the failure of acetic acid to enolize is ascribed, on modern theory, to the competition HO— C=O. There is no such competition in acetone, Me—C=O, and the latter reacts with halogens in its enolic form, slow enolization being followed by a relatively instantaneous reaction of the enolide with halogen. Similarly, enolization of the acyl halides should also be possible, and enolization will here be facilitated by the inductive effect of the halogen atoms.[4]
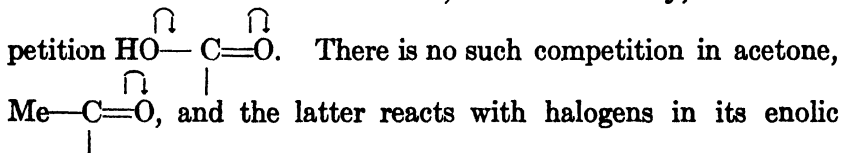
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[4] The relative inductive effects of methyl and halogen are exemplified by a comparison of the strengths of o-bromobenzoic (K = 1.215 × 10⁻³) and monobromoacetic (K = 1.5 × 10⁻³) acids with those of o-toluic (K = 1.2 × 10⁻⁴) and propionic (K = 1.34 × 10⁻⁵) acids; also in the increasing proportion of meta-derivative formed (see Baker and Ingold: J. Chem. Soc. **1926**, 2466) in the nitration of the series.
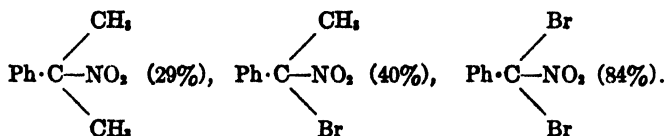
It is to be anticipated, therefore, that acetyl chloride and bromide will enolize at a much greater rate than does acetone. After enolization, the enolide will become activated as follows,

$$-\overset{\ominus}{\underset{\ominus}{C}}=\overset{\curvearrowright}{\underset{X}{C}}-\overset{\curvearrowright}{OH}; $$
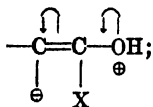
and this activation will now be opposed by the effect of the halogen. It may be predicted, therefore, that in the acyl halides rapid enolization will be followed by a relatively slow reaction of the enolide with halogen[5]; if this be the case, the velocity of halogenation will be proportional to the concentration of the halogen, as is found by experiment. The fact that substitution in aliphatic acids invariably occurs at the α-position finds a simple explanation in this suggestion. The relatively slow rate of halogenation of acetyl chloride (as compared with the acid bromide, see p. 185) is probably to be attributed to the greater inductive effect of chlorine than of bromine (4) (43).

Reactions (2) and (2a) (p. 184). The reaction of a carboxylic acid with the halide of another acid was observed by Polzenius (80), who isolated benzoic acid and acetyl chloride by distilling acetic acid with benzoyl chloride, and a similar reaction was suggested by Orton (70) as providing a possible explanation of the formation of acid amides, sometimes in 75 per cent yield, by the reaction of benzoyl chloride with carboxylic acids in presence of ammonia.

An investigation of the products of the reaction of acetic acid with its halogenated halides has indicated that these reactions

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[5] An analogy is found in the suggestion (West: J. Chem. Soc. **125**, 1277 (1924)) that, in the bromination of monobromomalonic acid, rapid enolization is followed by a slow reaction with halogen,

$$\text{HOOC·CHBr·COOH} \xrightarrow{\text{rapid}} \text{HOOC·CBr:C(OH)}_2 \xrightarrow{\text{Br}_2\text{ (slow)}} \text{HOOC·CBr}_2\text{·COOH} + \text{HBr.}$$
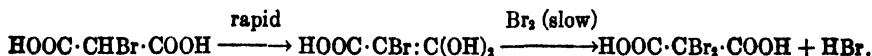
In order to account for the fact that the enolic forms of these compounds have never been observed, it is necessary to suppose that the change of enol to keto is extremely rapid.

occur in two stages, a mixed anhydride being formed as intermediate product, thus;

$$CH_2X \cdot COX + CH_3 \cdot COOH \rightleftharpoons CH_2X \cdot CO \cdot O \cdot CO \cdot CH_3 + HX$$
$$CH_2X \cdot CO \cdot O \cdot CO \cdot CH_3 + HX \rightleftharpoons CH_2X \cdot COOH + CH_3 \cdot COX.$$
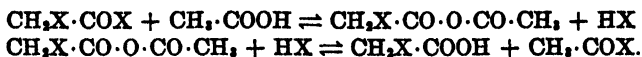
Thus, on distillation of acetic acid with chloroacetyl chloride, the first product is acetyl chloride, and if the remainder be fractionated under reduced pressure, acetic chloroacetic anhydride may be obtained. The mixed anhydrides undergo various changes according to the experimental conditions; they react with halogen acids (as above equation) with great readiness even at room temperature, and in the halogenation of acetic acid at 100° (when halogen acid is formed continuously) this change will doubtless be practically instantaneous.

The halogenation of carboxylic acids in presence of a trace of acyl halide has thus been shown to proceed through the series of reactions:

$$R \cdot CH_2 \cdot COX + X_2 = R \cdot CHX \cdot COX + HX$$
$$R \cdot CHX \cdot COX + R \cdot CH_2 \cdot COOH \rightleftharpoons R \cdot CHX \cdot CO \cdot O \cdot CO \cdot CH_2 \cdot R + HX$$
$$R \cdot CHX \cdot CO \cdot O \cdot CO \cdot CH_2 \cdot R + HX \rightleftharpoons R \cdot CHX \cdot COOH + R \cdot CH_2 \cdot COX.$$
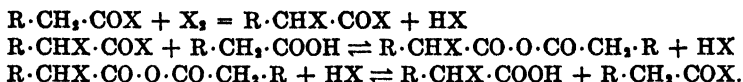
This scheme appears to be in harmony with all the experimental results.

Catalytic effect of phosphorus. The original Hell-Volhard reaction obviously consisted in the bromination of the acid bromide. The acid was treated with sufficient phosphorus and bromine for complete conversion to bromide and bromination of the latter, and the product was treated with water in order to obtain the halogenated acid. It was found, however, that a vast increase in speed of bromination was produced by a very small quantity of phosphorus, and the effect of the catalyst was here difficult to explain. Lapworth (53) suggested that it might be attributed to the production of hydrogen bromide which accelerated the enolization of the acid, but this idea has been shown to be untenable. Moreover, Ward's results (91) showed clearly that the catalytic effect of phosphorus is far more powerful than that of halogen acids; it is, in fact, of the same order of magnitude as that of acid bromides observed by the author. In bromination

in presence of phosphorus a small amount, at least, of the acid bromide is always formed, and may be detected in the product; it is quite obvious, therefore, that the acceleration is due to this small quantity of acid bromide, the reaction proceeding according to the scheme outlined above. The similar effect of phosphorus or phosphorus pentachloride on the chlorination of carboxylic acids (see Brückner (7)) may be interpreted in the same manner.

Catalytic effect of halogen acids. It may be further suggested that the effect of halogen acids is due to traces of the acyl halide present in equilibrium with the acid,

$$R \cdot COOH + HX \rightleftharpoons R \cdot COX + H_2O.$$
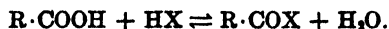
The very different effects of halogen acids and acyl halides indicate that the quantity of acyl halide necessary to produce the observed velocity would be too small for detection, and the existence of such an equilibrium has never been demonstrated. It is not impossible, however, in view of the reversible nature of the hydrolysis of many inorganic chlorides, while it is suggested by reactions of the type:

$$R \cdot CN + R' COOH + 2 HCl = R \cdot CO \cdot NH_2 \cdot HCl + R' \cdot COCl$$
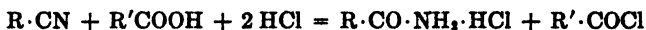
(Colson (13)). Such an interpretation is supported by the following facts:

(*a*) the influence of halogen acids is specific, and not common to acids in general;

(*b*) Lapworth observed that a small quantity of water (which would displace the above equilibrium towards the left-hand side, thus reducing the concentration of acyl halide) reduces very considerably the speed of bromination, and this result has been confirmed by the author;

(*c*) when varying amounts of the acid bromide are added to acetic acid containing a small amount (e.g., 0.1 per cent) of water, there is a continuous increase in velocity as the amount of acid bromide becomes greater, and not a sudden increase at the point where the bromide is just in excess of the water; addition of anhydride, on the other hand, causes a sudden increase at this point.

In the former case, therefore, a gradual increase in the amount rather than a sudden change in the nature of the catalyst is indicated.

The above suggestion brings into harmony all previous observations of the catalyzed halogenation of carboxylic acids, by postulating in every case a similar mechanism, viz., the series of reactions involving the halogenation of the acyl halide.

Dicarboxylic acids. The results outlined above indicate clearly that acetic acid and its homologues show little or no tendency to enolization. It is obviously necessary to explain the fact that malonic acid is known to react with bromine in its enolic form (64) (99). As in the case of acetic acid, there is here the competition COOH $-$ CH$_2$ $-$ C$\diagup^{\displaystyle O}_{\displaystyle OH}$, which, as already pointed out, neutralizes the effect of the partial appropriation of electrons by the carbonyl oxygen, and removes (in the case of acetic and homologous acids) the tendency of the α-hydrogen atom to ionize. In malonic acid, however, there is also the powerful inductive effect of the second carboxyl group (compare p. 179), and it is doubtless this influence which causes enolization to take place readily even at temperatures as low as 0°. In the case of monobromomalonic acid, the combined effects of the carboxyl group and the bromine atom tend in this direction, and it appears (99) that here the rate of enolization is very rapid in comparison with the speed of reaction of the enolide with bromine.

Succinic acid is known to react with bromine in aqueous solution at temperatures above 100°; the conditions are obviously unfavorable to the production of the acyl halide, and it may be suggested that here also the acid reacts in its enolic form. If this be the case, enolization occurs less readily than in the case of malonic acid, since a much higher temperature is needed for bromination, and this may be ascribed to the screening effect of the second carbon atom (compare p. 179). Succinic acid is brominated far more rapidly by the Hell-Volhard method, however, and it may be inferred that, as in the case of the monocar-

boxylic acids, the acid bromide enolizes with greater ease than the acid itself.

If these suggestions be correct, further increase in the length of the chain between the carboxyl groups should result in a progressive decrease in the speed of bromination, and it is significant that there is no reference in the literature to the bromination of glutaric and the higher acids in aqueous solution, although these acids may be brominated by the Hell-Volhard method. The bromination of dicarboxylic acids is now being further investigated.

III. ACID ANHYDRIDES

The results of certain experiments carried out in this laboratory during the period 1911–14 (71) (33) (73) led to the conclusion that pure acetic anhydride is unattacked by halogens at the ordinary temperature when light is completely excluded, but that the presence of very small quantities of various foreign substances induces a fairly rapid reaction. The observations were not in harmony with the work of earlier investigators (Gal (30); Urech (90); Lapworth (53)), who state that the anhydride reacts, in absence of a catalyst, to give acyl halide and monohalogenated acid,

$$(CH_3 \cdot CO)_2O + X_2 = CH_3 \cdot COX + CH_2X \cdot COOH.$$

It was significant that all the experiments in which the anhydride was found to be stable to halogens were carried out with the same batch of Kahlbaum's acetic anhydride "free from homologues," purified by fractional distillation, and in order to test the truth of the conclusion reached, an examination was made of the stability to bromine of specimens of acetic anhydride of varied origin and purified by different methods (74). In every case reaction occurred, and it appears probable that the material employed by the pre-war workers contained a trace of some inhibitor which was not removed by fractionation. A search for possible inhibitors has revealed the fact that the introduction of quinoline in minute quantity prevents the reaction from proceeding to a perceptible extent during a long interval of time (in an experiment

using $Br_2 = 0.25M$ and $C_9H_7N = 0.006M$ the latent period was of ninety-three hours' duration), after which a fall in bromine concentration commences. Moreover, acetic anhydride containing a trace of quinoline is still stable to bromine after fractionation. Sodium acetate exerts an influence which is similar to, but not as powerful as that of quinoline, whilst (in descending order) pyridine, dimethylaniline, triethylamine, isoquinoline, ammonium acetate, methylamine and ethylamine are less effective. Addition of a trace of nitric acid or of acetyl nitrate is accompanied by an extremely powerful inhibition; the effect of the former is probably due to acetyl nitrate formed (79) by reaction of the acid with acetic anhydride, for the bromination of propionic anhydride (which is similar to that of acetic anhydride, but considerably slower) is inhibited by acetic anhydride and nitric acid in conjunction but not by nitric acid alone. It is remarkable, however, that these substances which inhibit the bromination of acetic anhydride have no similar effect on the chlorination of the same substance. This peculiarity is discussed later.

The mechanism of the reaction. The idea that the reaction of chlorine or bromine with acetic anhydride (to give acyl halide and monohalogenated acid) might occur in more than one stage is due originally to Lapworth (53), who discovered that the introduction of mineral acid led to an increase in speed, and suggested (by analogy with the bromination of acetone) that halogenation might be preceded by enolization of the anhydride. The results of Orton and Jones (71) appeared to indicate that the speed of halogenation in presence of a catalyst was independent of the concentration of halogen, and thus to confirm Lapworth's suggestion. Fuller investigation (74) (97) of the reaction of chlorine and of bromine with acetic anhydride at 25°, however, has shown that the velocity is very greatly influenced by changes in the concentration of halogen, and, moreover, is increased by the presence of an acyl halide. The effect of halogen acids is identical with that of acyl halides, owing to the conversion (all but complete)

$$(CH_3 \cdot CO)_2O + HX \rightleftharpoons CH_3 \cdot COX + CH_3 \cdot COOH.$$

Chlorination is a much slower process than bromination.

These observations recall the halogenation of carboxylic acids (preceding section), and suggest a series of changes of the following type;

$$CH_3 \cdot COX + X_2 = CH_2X \cdot COX + HX \qquad (1)$$
$$(CH_3 \cdot CO)_2O + CH_2X \cdot COX \rightleftharpoons CH_2X \cdot CO \cdot O \cdot CO \cdot CH_3 + CH_3 \cdot COX \qquad (2)$$
$$(CH_3 \cdot CO)_2O + HX \rightleftharpoons CH_3 \cdot COX + CH_3 \cdot COOH \qquad (5)$$
$$CH_3 \cdot COOH + CH_2X \cdot CO \cdot O \cdot CO \cdot CH_3 \rightleftharpoons CH_2X \cdot COOH + (CH_3 \cdot CO)_2O \qquad (6)$$
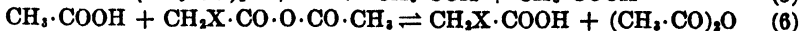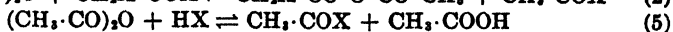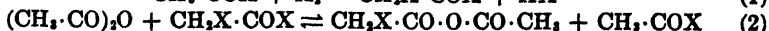
preceded, if the halide of another acid is added initially, by

$$(CH_3 \cdot CO)_2O + R \cdot COX \rightleftharpoons CH_3 \cdot CO \cdot O \cdot CO \cdot R + CH_3 \cdot COX,$$

or

$$(CH_3 \cdot CO)_2O + 2 R \cdot COX \rightleftharpoons (R \cdot CO)_2O + 2 CH_3 \cdot COX.$$
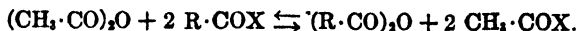
Reactions similar to (6) have been observed by Kaufmann and Luterbacher (49), and the reactions of acetic anhydride with certain acyl halides have been carried out by the author, who finds, for example, that when the anhydride is distilled with chloroacetyl chloride, the products are acetyl chloride and either acetic chloroacetic anhydride or chloroacetic anhydride, depending upon the relative proportions of the reagents.

In the above series of reactions, the rate of disappearance of halogen will be

$$dx/dt = k (a - x) \text{ [acyl halide]}$$

where a is the initial concentration of halogen. If the acyl halide be present in excess, the reaction will be of the first order; the calculated values of

$$k_1 = 1/t \cdot \log_e a/a - x,$$

however, are not constant. If the halogen also reacts with the enolic form of the anhydride (this form being produced slowly and reacting with halogens rapidly), the rate of disappearance of chlorine or bromine will be

$$dx/dt = k(a-x) \text{ [acyl halide]} + k' \text{[anhydride]},$$

where x is the total amount of the halogen which reacts in time t. In the case where both acyl halide and anhydride are in excess, this reduces to

$$dx/dt = C(a-x) + C' = C(a-x+P), \text{ where } C' = CP,$$

which on integration becomes

$$C = 1/t \cdot \log_e (a+P)/(a+P-x).$$

Constant values of C are obtained by the use of this expression, and the calculated values of k' are the same for both chlorination and bromination. The side reactions which have been observed to take place during the chlorination of acetyl chloride (p. 185) are here not perceptible, owing to the relatively great speed of reaction of chlorine with the acid chloride in acetic anhydride medium (see p. 195).

The results indicate, therefore, that the halogenation of acetic anhydride proceeds by two routes, A and B, as follows;

(A) $CH_3 \cdot COX + X_2 = CH_2X \cdot COX + HX$ (1)

    $(CH_3 \cdot CO)_2O + CH_2X \cdot COX \rightleftharpoons CH_2X \cdot CO \cdot O \cdot CO \cdot CH_3 + CH_3 \cdot COX$ (2)

(B) $(CH_3 \cdot CO)_2O \rightleftharpoons CH_2 : C(OH) \cdot O \cdot CO \cdot CH_3$ (3)

    $CH_2 : C(OH) \cdot O \cdot CO \cdot CH_3 + X_2 = CH_2X \cdot CO \cdot O \cdot CO \cdot CH_3 + HX$ (4)
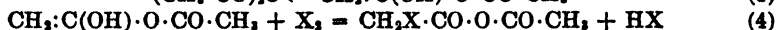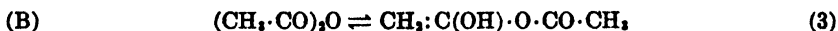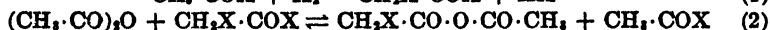
the ultimate products then being formed by the further reactions

$$(CH_3 \cdot CO)_2O + HX \rightleftharpoons CH_3 \cdot COX + CH_3 \cdot COOH \quad (5)$$

$$CH_3 \cdot COOH + CH_2X \cdot CO \cdot O \cdot CO \cdot CH_3 \rightleftharpoons CH_2X \cdot COOH + (CH_3 \cdot CO)_2O \quad (6)$$
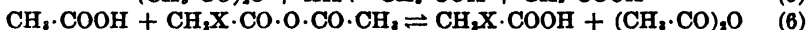
Route A is the more rapid. The difference in speed between chlorination and bromination is due entirely to the difference in the velocities of halogenation of the acyl halides (compare p. 185).

The fact that acetic anhydride enolizes more readily than acetic acid may be attributed to the sharing of the influence of the singly linked oxygen by the two carbonyl groups,
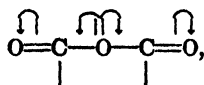
an effect which is described by Robinson (83) (55) as a "side tracking by a neighboring system of high capacity," and the result is a less complete neutralization of the effect of the carbonyl oxygen. The halogenation of the anhydride, unlike that of acetic acid, is accelerated powerfully by small quantities of sulfuric acid or ferric chloride; the effect of these substances consists in a speed-

ing up of the enolization of the anhydride, for they have no effect on the halogenation of the acyl halide.

It has thus been demonstrated that the reactions of the halogens with carboxylic acids and with acid anhydrides involve similar series of changes, viz., the halogenation of the acyl halide, followed by an interaction of the substituted halide with the acid or anhydride. In the case of the anhydrides, however, the reaction proceeds readily at 25°, while a much higher temperature (e.g., 100°) is required for the halogenation of the acids. This difference appears to be due to the effect of the medium on the velocity of halogenation of the acyl halide, acetic anhydride being a much more favorable medium than acetic acid. Such an explanation is confirmed by the author's observation that addition of a small quantity of acetic anhydride to acetyl bromide results in a great increase in the speed of bromination, whereas the acid bromide reacts with bromine but slowly in acetic acid medium at 25°, and not perceptibly in media such as carbon tetrachloride. The halogenation of the anhydrides of carboxylic acids is thus, in general, analogous to that of the acids themselves, although there are various differences in detail.

The inhibition of bromination. The peculiar effect of quinoline and other substances, which has been referred to above, may be interpreted on the basis of the mechanism which has now been established for the reactions of the halogens with acetic anhydride. In order to throw further light upon the action of quinoline, its effect on the bromination of acetone has been studied (94). When bromine is added to acetone in carbon tetrachloride medium at 25°, no measurable reaction occurs for a short time (which is of variable duration, see p. 176); the disappearance of bromine then becomes perceptible, and almost immediately attains great speed, owing to the very powerful catalytic effect of hydrogen bromide upon enolization in non-ionizing media. Addition of a trace of quinoline arrests the reaction during a long period (several days; the arrests are immensely greater than those referred to on p. 175), and it seems simplest to suggest that the arrest is due to the removal of hydrogen bromide as the hydrobromide (or hydrobromide perbromide (34) (89)) of the base. The well-known

inhibition, by certain nitrogen-containing compounds, of gaseous photochemical reactions, has been interpreted in terms of the energetics of the system (11) (12), and of surface phenomena (69), and K. C. Bailey (2) has suggested that the inhibition of esterification by pyridine is due to the preoccupation of active points of the glass surface of the vessel by pyridine molecules, which remove the molecules of acid from postulated acid-alcohol complexes. The author's view of the case under discussion appears, however, to account for the observed facts, and it is immaterial whether the reaction occurs at the surface of the vessel or in the body of the liquid.

A similar interpretation may be applied to the case of acetic anhydride. The reaction of the base with the halogen acid produced in the bromination of the enolized anhydride will prevent the formation of any appreciable quantity of acetyl bromide (or perhaps any acid bromide formed may be converted into an additive compound with quinoline (19)); the main series of reactions, which involves the bromination of the acid bromide, is thus eliminated, until sufficient hydrogen bromide has been formed (in the slow change through the enolized anhydride) to react with the whole of the base. If, however, in presence of quinoline, the enolization of the anhydride took place at the rate indicated by the values of k' referred to on page 193, the small quantities of the inhibitor employed would be removed in a few minutes, whereas the arrests observed are of many hours' duration. In the absence of an inhibitor, however, a small quantity of hydrogen bromide is always present in the equilibrium

$$(CH_3 \cdot CO)_2O + HBr \rightleftharpoons CH_3 \cdot COBr + CH_3 \cdot COOH,$$

and since acetic anhydride behaves in all respects as a "normal" liquid (compare D. C. Jones and Betts (48); D. C. Jones (47)), this halogen acid will be present in the covalent form; a very minute quantity will therefore produce a marked acceleration of the enolization (compare p. 177). Removal by quinoline of the greater part of this hydrogen bromide will render the enolization of the anhydride so slow as to be imperceptible, and the prolonged period of inertness is thus explained. The shorter duration of

this period in presence of pyridine, isoquinoline, triethylamine and dimethylaniline may be attributed to a larger amount of hydrogen bromide present in equilibrium with the base and its hydrobromide, $B \cdot HBr \rightleftarrows B + HBr$. The relatively feeble effect of aliphatic primary and secondary amines is to be expected, since they can be acetylated by the anhydride, as is also the complete inactivity (and even slight accelerating influence) of aniline and monomethylaniline, which are not only acetylated but also substituted in the benzene nucleus, with production of hydrogen bromide.

The negative catalytic effects of organic bases on the bromination of acetic anhydride may be ascribed, therefore, to the removal of hydrogen bromide (or perhaps sometimes of acetyl bromide) by combination with the base. The series of reactions involving the acid bromide is thus eliminated, and, in addition, the speed of enolization of the anhydride very considerably decreased. Sodium and ammonium acetates produce a similar effect owing to the reaction

$$CH_3 \cdot COOM + HBr = CH_3 \cdot COOH + MBr,$$

which proceeds further in the case of the former, as is indicated by its superior inhibiting action.

Even more remarkable than the inhibition of the bromination of acetic anhydride by these basic substances is the fact that they have no similar effect upon chlorination; an explanation of this unexpected difference may be found, however, in the following considerations. Since in acetic anhydride medium the halogen acids are doubtless covalent compounds, their reaction with a base must consist in the giving up of a proton covalently linked to the halogen, and if such release of the proton is not possible no reaction with the base will occur, and halogenation will not be inhibited. It is well-known that in presence of an excess of bromine, hydrogen bromide exists almost entirely as the perbromide HBr_3; the powerful electron affinity of the two coördinated bromine atoms (compare p. 178) will bring about a loosening of the proton, thus enabling its appropriation by the base to take place

readily. The reaction of quinoline with the acid is therefore represented

$$\begin{array}{c}-C\\ \diagdown\\ \diagup\\ -C\end{array} N: \;+\; H\!:\!\ddot{Br}\!:\!(Br_2) \;\rightarrow\; \begin{array}{c}-C\\ \diagdown\\ \diagup\\ -C\end{array} N\!:\!H^{+} \;+\; :\!\ddot{Br}\!:\!(Br_2)^{-}.$$
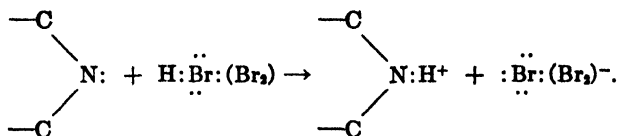
An analogy, consisting in the withdrawl of a proton covalently attached to oxygen, is found in the production of hydroxo-ammines of cobalt and chromium by the action of pyridine or ammonia on the corresponding aquo-ammines (98) (77), as exemplified in the reaction

$$[Cr(NH_3)_2(H_2O)_4]\,Cl_3 + 2\,C_5H_5N = [Cr(NH_3)_2(H_2O)_2(OH)_2]\,Cl + 2\,C_5H_5N \cdot HCl.$$
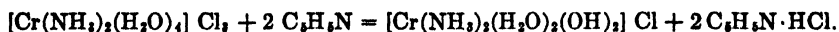
In the case of hydrogen chloride, there is but little perhalide formation (compare the relative effects of hydrogen chloride and bromide on the chlorination and bromination respectively of acetanilide (72)); weakening of the covalent bond does not therefore occur, and the base has no opportunity of combining with the proton. The hydrogen chloride is thus free to react with a molar quantity of anhydride

$$(CH_3 \cdot CO)_2O + HCl \rightleftharpoons CH_3 \cdot COCl + CH_3 \cdot COOH;$$

the chlorination of the acid chloride then proceeds, and, moreover, the enolization of the anhydride is catalyzed not only by the small quantity of halogen acid present in the above equilibrium, but also by the base (the latter being, however, comparatively insignificant). Chlorination is therefore not inhibited, but to some extent accelerated.

The effect of acetyl nitrate on the bromination of acetic anhydride may also be ascribed to the removal of hydrogen bromide (or perhaps of acetyl bromide), in this case by oxidation, for there is considerable liberation of bromine when acetyl bromide is added to acetic anhydride containing nitric acid. As in the case of the basic substances, the main series of reactions will thus be eliminated, and the enolization of the anhydride rendered impercep-

tibly slow.   As might be expected, however, from the relative indifference of hydrogen chloride to oxidizing agents, acetyl nitrate does not inhibit chlorination.

CONCLUSION

The investigation, described in the preceding pages, of the reactions of chlorine and bromine with compounds containing the carbonyl group, has led to a confirmation of the idea, suggested originally by Lapworth, that these changes are preceded, in all cases, by the conversion of the carbonyl compound to its enolic isomeride.   In the case of ketones and ketonic acids, slow enolization is followed by a relatively instantaneous reaction with the halogen.   Acetic acid and its homologues, on the other hand, do not enolize to a perceptible extent.   Their substitution products result from the reaction of the acid with its monohalogenated halide, the latter being formed, however, by a process which appears to consist in rapid enolization of the unsubstituted chloride or bromide, followed by a slow reaction of the enolide with halogen.   Acid anhydrides react with halogens in their enolic forms, but here also the change proceeds mainly through the acyl halide.

All the experimental results are such as would be anticipated from theoretical considerations involving the application of the electronic theory of valency, while the well-known fact that substitution invariably occurs at the α-carbon atom receives a simple explanation.

In conclusion, the author wishes to place on record his indebtedness to the late Professor Kennedy Orton, M.A., Ph.D., F.R.S., whose helpful and inspiring advice and criticism have contributed in no small degree to the success of the series of investigations here described.

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CHEMICAL ACTIVATION BY LIGHT AND BY IONIZING AGENTS

INTRODUCTION TO SYMPOSIUM ON RADIATION [1]

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In recent years much light has been shed on the subject of chemical kinetics from quite varied sources—partly classical and partly new. As a whole the subject does not reveal itself as a simple one. Much of the progress that has been made is of orientative character and most details yet remain to be worked out and fitted to general schemes. Nevertheless it is perhaps not too much to claim that we begin to get an outline of the underlying principles of chemical activation from the least to the most energetic types. The working out of a complete mechanism is a special problem for each reaction, and there seems to be no end to the variations that are encountered.

As indicated in its title, the object of the present Symposium was to consider mainly the more vigorous types of activation, as they are represented in the phenomena of ionization, on the one hand, in the complete removal of an electron from one of the reactant molecules or, on the other hand, in photochemical excitation as represented in the orbital shift of an electron, sometimes followed by dissociation.

Although only part of the papers presented at the Symposium are contained in this issue of CHEMICAL REVIEWS, reference will be made to some of the others, which have been published elsewhere. Also, for the sake of completeness, certain phases of the less vigorous types of reactions as represented in homogeneous thermal reactions will be discussed as an introduction to the

present status of chemical kinetics. Chain mechanism may be initiated by either type of activation, and hence is appropriately considered. The comparison of temperature coefficients of velocity in the various cases is also illuminating.

The greatest difference between thermal reactions and photochemical or ionochemical ones is in the quantity of energy involved in the primary activation process. In thermal reactions the heats of activation are from 21,000 to 58,000 calories for second order reactions, while for first order reactions they extend over about the same range, 24,700 to 68,500 calories, or in both cases from 1 to 3 electron-volts; while in activation involving electron shift or removal, the energy is 5 to 15 electron-volts. In bimolecular thermal reaction this critical energy increment above the average energy content may be distributed presumably in any proportion between the two colliding molecules, principally in the form of kinetic energy. The molecules which react directly in this way have been found to be of a rather simple character, that is, possessing a limited number of atoms and a correspondingly small number of degrees of freedom to withstand shock and to store energy in a latent form.

Unimolecular reaction, on the other hand, is exhibited by more complex molecules with a large number of degrees of freedom in which activation energy is accumulated (or lost) by successive collisions and stored for the critical condition of dissociation or change. It is not quite so obvious why the heat of activation should be of the same order for this type of activation as for the bimolecular type (1). However, the difficulty of explaining the mode of activation in unimolecular reaction has been largely overcome by Lindemann's suggestion of successive accumulation and storage, so that there is no direct relation between rate of storage and rate of reaction as long as most of the stored energy leaks away by the reverse process of deactivation.

In any case we are no longer under the necessity of resorting to the radiation hypothesis to account for unimolecular reaction. In this connection it is interesting to have the most recent views of F. Perrin (p. 232), who points out that although activation and fluorescence are in general opposing influences, yet, according to

the principles of microscopic reversibility of equilibrium, where one exists the other must be possible; and since fluorescence in the infra-red region is rare or unknown, energy of activation by collision ought to be especially available.

The conception of chain mechanism, originally proposed by Bodenstein in the case of the photochemical interaction of hydrogen and chlorine has proved highly useful, and in more recent times is being extended to thermal reactions on the one hand and to ionic[2] ones on the other. Semenoff has used thermally initiated chains and the breaking of chains to distinguish a type of explosion different from the ordinary thermal type, which is characterized by its dependence on the size and shape of the vessel, thus giving a spatial reality to the chain conception.

Chain mechanism has been successfully used to establish reaction mechanism involving intermediate processes. The two outstanding examples of chain mechanism in photochemical reactions are the syntheses of hydrogen chloride and of phosgene. In the former we still have two possible types of chain reaction to decide between,—the material chain of Nernst on the one hand, which assumes the production of Cl atoms which are used and regenerated in each cycle, and the energy chain of Bodenstein which assumes that only the heat of reaction is passed on by collision from freshly formed "hot" molecules to activate the reactants. The selectivity which this latter mechanism requires in the presence of foreign or product molecules begins to appear possible through the resonance relations of wave mechanics. Such a selectivity of transfer also appears necessary in chain reactions in solution, to avoid the problem of deactivation by the solvent.

In phosgene synthesis a still more complicated case is presented in which even the mechanism seems to change with temperature. Prof. Bodenstein has presented the latest views in his paper on this subject (p. 225). A universal mechanism for the phosgene reaction has not yet been worked out, but such progress has been

[2] The discovery of the great excess of hydrogen chloride molecules formed over the number of *ions* under alpha radiation of $H_2 + Cl_2$ mixture slightly antedated Bodenstein's photochemical work and was cited by him in support of his first "electron" chain mechanism.

made as to justify the hope of a definite solution in the near future.

The syntheses of HCl and of $COCl_2$ have also been investigated under alpha radiation and have disclosed a complete parallelism with the photochemical processes. The first investigation of the $H_2 + Cl_2$ reaction under alpha radiation by Bodenstein and Taylor disclosed a large excess of action over ionization ($M/N = 4,000$) but nevertheless far below that in the photochemical reaction ($M/h\nu = 10^5 - 10^6$), to be understood on account of variation in sensitivity. The work of Porter, Bardwell and Lind raised the M/N value to nearly four times the $M/h\nu$ value as determined in a gas mixture of the same sensitivity, but the latest work of Lind and Livingston (2) reported in this Symposium shows that within experimental limits of error $M/N = \dfrac{M}{h\nu}$, for all sensitivities. The method of work did not permit of investigating the reaction mechanism with respect to other than equivalent concentrations of Cl_2 and H_2. The work of Alyea and Lind (3) on phosgene synthesis under alpha radiation shows that the kinetics are identical with those found by Bodenstein and co-workers for its photochemical synthesis, both with respect to the rate, which is proportional to the square root of the intensity of radiation, and with respect to the concentrations of both CO and Cl_2. The chain length is also of the same order as under the influence of light and also subject to the same degree of inhibition by oxygen.

The equality of M/N and $M/h\nu$ extends also to the non-chain types of reaction, of which about a half dozen cases have now been quantitatively investigated by means of both agents of activation. Each new reaction investigated or each increase in accuracy for old ones establishes this equality more firmly and brings us face to face with the problem of a mechanism to provide a step that will lead to a common course from that point on. It is to be remembered how different the agents are, one an atomic particle of high velocity with a universal ionizing power toward all atoms and molecules in proportion to the two-thirds power of the concentration of their orbital electrons, while the photochemi-

cal agent is highly specific, dependent on its wave length, toward absorption by and action on different atoms and molecules. The primary activation step consists then of ionization, or the removal of an electron in one case, and of the orbital displacement in the other. It is not immediately apparent why the two types should lead to the same kind and amount of reaction, but it is clear that they may do so.

In the ionic reaction it has proved useful to assume that the molecular ions of one of the reactants collects by electro-dynamic induction other neutral molecules into a positive (or sometimes negative) cluster, which undergoes chemical reaction upon final electrical neutralization (return of the electron). From the known rate of ion recombination, it may be calculated that a large number of collisions of neutral molecules with an ion would take place before its neutralization occurs. It has been suggested (4) that even in the case of the excited state, its duration and electrical moment would be sufficient to account for "photochemical clustering", which would then furnish a common basis for the iono- and photo-chemical types of reaction. The main objection to the clustering hypothesis is that we have no definite knowledge of the actual existence of such ion clusters and certainly none of the photochemical ones. But we do know that as many as twenty acetylene molecules condense per ion pair into a solid polymer, presumably of high molecular weight, and it appears easier to assume that this collecting action proceeds under an electrical attraction, rather than by some step process after that attraction has been removed.

The alternate view (5) is that dissociation into atoms and free radicals, or possibly activation without such dissociation, takes place in the primary step in both cases, to be followed then by the ordinary thermal behavior of the primary products. The question is really very much like the time-honored one of intermediate addition products versus primary dissociation. We have perhaps in the newer cases additional points of attack that will enable a definite decision, but up to the present they have not been sufficiently developed and we have only indirect evidence, some of which favors the one view and some the other. For

example, the fact that both the kinetics and the quantum yields indicate the identity of the mechanisms for the photo- and iono-reactions in the syntheses both of hydrogen chloride and of phosgene certainly appears to support the view of Taylor and Jones. On the other hand, when one has a straight reaction of polymerization as in the cases of acetylene, cyanogen etc., where there is little evidence of primary splitting and where the final products represent a much higher degree of association than in the initial state, one is forced to choose between ion clustering and some type of step reaction following ion recombination. One can assume that the heat of ion recombination becomes available for activation in some way, but must face the problem that this activation must be followed by a clustering process and without the aid of any electrical attraction, or else by step-wise accretion to a critical size, with no characteristics of chain mechanism exhibited, such as inhibition, variable yield etc. In the polymerization cases the choice appears to favor electrical clustering rather than the apparently more artificial step-mechanisms.

It is by no means impossible that the primary mechanism may be dissociation in some cases and clustering in others. Modern kinetics show us that the same reaction product may be arrived at in different ways.

Another common property of photo- and iono-chemical action is activation by means of sensitization through a non-reactant which receives the energy and imparts it to the reactant in a collision of the second kind. Owing to the selective nature of photochemical action, the sensitized reaction may represent the sole one occurring for a given wave length. But since no substance is transparent to alpha rays, the sensitized reaction in that case will not be exclusive but will always be added to the direct activation of the reactant. The sensitized fraction may, however, become very large where the concentration of reactant falls very low in comparison with that of the sensitizer.

In the ionochemical gaseous reactions one has a new principle entering,—namely, transfer by collision of positive charge to the component gas with lowest ionization potential. It has been found that even when the transfer is to a foreign inert gas, poly-

merization about the foreign ion occurs to the same degree as about a reactant one. This appears good evidence in favor of clustering about the foreign ion.

The advantage which alpha radiation has over other ionizing agents is that it can be produced by means of radon under such conditions, even at ordinary and higher pressures, that the total ionization is readily calculated. Therefore comparison of ionization and chemical action becomes possible, as expressed in the M/N ratio. In other modes of ionization, such as electrical discharge in gases and by means of cathode rays, it is not usually possible to calculate the ionization. The fact, however, that the nature of the products and of their proportions to each other—in a reaction yielding several products—are the same for the same gas both under alpha radiation and under electrical discharge, supports the view (6) that ionization is the primary step in both cases. Substantial progress has recently been made in calculating and measuring ionization also in electronically produced chemical action. Busse and Daniels (7) have passed a stream of cathode rays from a Coolidge tube through a thin window into oxygen where the ozone could be measured chemically; the ionization was calculated by receiving the cathode rays in a total absorption calorimeter to measure their total energy. By assuming the energy to have been primarily expended entirely in ionizing oxygen with an expenditure quantized by its known ionization-potential, a value of M_{O_3}/N ions was obtained which by its agreement with the alpha ray value demonstrated the reliability of the method.

In glow discharge at pressures of a few millimeters by suitable choice of electrode dimensions and separation, saturation is obtained so that the current flowing becomes a measure of the total ionization. Working under these conditions, Brewer (8) and his associates of the Fixed Nitrogen Laboratory have measured several gaseous reactions such as the syntheses of ammonia, of water and of nitrogen dioxide from their elements, and have found the same degree of equivalence between ionization and chemical action as was to be expected from the alpha ray results in the same cases. They propose a very clever and apparently

satisfactory interpretation,—namely, that the chemical action is due to the positive ions, while the electrical current is carried almost wholly by the free electrons due to their greater mobility. In saturation current the two are equal to each other, and therefore the amount of chemical action is equivalent to the current and independent of the gas pressure as long as the latter is kept within low limits where saturation is obtained. If the pressure is allowed to rise to values where recombination of ions in the gas phase exceeds discharge at the electrode, then chemical action associated with ion recombination will exceed the current equivalent. This is the usual case represented in all types of electrical discharge at atmospheric pressure, where the chemical action greatly exceeds the current equivalent.

In the general comparison of chemical action in gases under electrical discharge and under alpha radiation, it might be logically assumed that if action is due to ions and if the ions are of the same character in both cases the nature of the resulting chemical products should be the same. While this is true in general, as is shown by comparison of the results obtained for hydrocarbon gases by Lind and Bardwell for alpha radiation and by Lind and Glockler for electrical discharge, nevertheless unexplained exceptions are met. For example, polymerization of acetylene gives solid cuprene under alpha radiation, but according to Berthelot it gives a liquid product like benzene in silent discharge. To explain these differences it is to be remembered that even if the ions produced are of the same kind, their concentration, and hence their rate of recombination, is far greater in electrical discharge than can be produced with any attainable alpha radiation. Moreover, in electrical discharge there exists the possibility of the influence of the electrode either electrically or catalytically, especially if it be a metal. The concentration of ions may have a large influence since recombination is a second order reaction, so that if the concentration be a thousandfold greater in electrical discharge than in alpha radiation, the rate of recombination becomes a millionfold greater, hence the average life of an ion a millionfold less, which brings it into a region where there will be serious competition between premature ion neutralization—lead-

ing to lower molecular weight products—and complete cluster building. While, as explained, we can not calculate ionization in the higher ion concentrations, we may as a first approximation assume it to be proportional to the chemical action and may reverse the calculation. The formation of benzene, a lower polymer than cuprene, could then be understood as a result of premature ion neutralization. If this principle could be established firmly in a number of cases it would be a strong support of ion clustering versus dissociation or thermal activation as a result of ion recombination.

It is well known that many photochemical reactions exhibit very small temperature coefficients. The same is true of the ionochemical reactions to an even greater degree, and for the same general reason that the energy of the primary step of activation by excitation or by ionization so far exceeds the necessary energy for activation that additional thermal energy is not required and will not influence the rate. This general statement of principle requires extension. In chain mechanism where the primary photochemical or ionochemical step is succeeded by thermal steps, it is evident that temperature may have an influence, and correspondingly we find the chain syntheses of HCl and COCl$_2$ exhibiting fairly large temperature coefficients (though much lower than those of purely thermal reactions). An additional proof of the identity of the chain mechanism of HCl synthesis by light and by alpha rays lies in the identity of the temperature coefficients for white light and for alpha rays. While this appears to contradict Tolman's principle that light of the longer wave length should exhibit the greater temperature coefficient, in reality it does not do so. An experiment of Lind and Livingston with monochromatic green light showed a somewhat higher coefficient than with white light and with alpha rays, but the proportion of green in the white source was so small that it cut but little figure in the over-all coefficient. It does mean, however, that it is inappropriate to choose a chain reaction to test the validity of Tolman's principle, because temperature can play a rôle in so many ways besides in the primary step with which one is solely concerned.

Regarding the temperature coefficient of radiochemical action in general; (*1*) temperature may, and sometimes does, affect directly the absorption of light of a given wave length by a given substance but not that of alpha rays; (*2*) temperature may and does affect the quantum efficiency of the primary activation step for light especially on the long wave length side of the critical value according to Tolman; this is not probable for ionization except at quite high temperature; (*3*) temperature may affect any succeeding step following the primary one; in chain reactions of several steps, each may be affected and some of them in opposite directions; the same would hold equally for the same chains initiated by ionization or by other agents. The temperature coefficient is therefore seen in complex cases to be made up of the algebraic sum of the coefficients of all steps. The fact that the coefficient of water synthesis by alpha rays is zero over a wide temperature range appears therefore to be evidence against the yield of four molecules per ion pair being accounted for by thermal processes succeeding primary ionization.

Further progress in photochemical and radiochemical effects on solids has been made (see p. 239). The primary effects do not appear to be of very different character from those observed for liquids and gases. But the opportunity for secondary effects and particularly for reverse reaction are profoundly modified by the rigidity of the solid system and its influence on diffusion of products and reactants. The result reported by Noyes (*loc. cit.*) that controlled electrons must have a voltage of 4.5 to 5.5 in order to decompose oxalic acid and that through the relation $e V = h\nu$, the effective wave length of light may be calculated and is experimentally found to lie near the threshold value, illustrates a direct application of quantum principles to radiochemical problems.

A very interesting region of photochemistry lies in the x-ray range, where but little quantitative work has been done. Here the energy quantum is so large that an electron is expelled with sufficient velocity to produce several thousand ion pairs in its small sphere of influence. We should therefore no longer expect equivalence between M, the reacting molecules, and number of

quanta hν in the Einstein sense as for smaller frequencies, but rather equivalence of M and the number of ion pairs N in the same way as in alpha ray reactions. Recent work by Clark, by Stenstrom (9) and by Fricke and Morse (10) has shown the latter to be the case.

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CHAIN REACTIONS

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The assumption of chain reactions was first used by me in 1913 (1) to interpret the fact that in many photochemical processes the number of reacting molecules is much larger than the number of absorbed quanta. I assumed that by the reaction of the primary light-affected molecule there is formed an unstable intermediate product, rich in energy, which on further reaction gives rise not only to the well-known final product, but also to another intermediate product which regenerates the same process again and again, thus producing a great number of molecules of the final product, starting from one quantum absorbed.

The simplest example is the mechanism proposed later by Nernst for the formation of hydrogen chloride:

$$Cl_2 + E^1 = 2\ Cl$$
$$Cl + H_2 = HCl + H$$
$$H + Cl_2 = HCl + Cl....$$
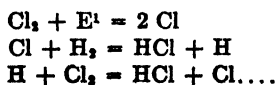
That indeed the "Chlorknallgas" gives such a long series of reactions has been shown most clearly by Weigert and Kellermann (2). After an illumination of 10^{-6} seconds they were able to observe a reaction during 2×10^{-2} seconds.

Such a chain may be produced in another way than by active intermediate products. The molecules of the final product must have an excess of energy immediately after their formation. By transferring this energy to the molecules of the starting material,

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[1] E means one Einstein = 6.06×10^{23} quanta, in analogy to F = one Faraday = 6.06×10^{23} electrons. See Bodenstein and Wagner: Z. physik. Chem. **B3**, 456 (1929).

they may activate these also.   Using the same example as before, the series would be:

$$Cl_2 + E = Cl_2^{*2}$$
$$Cl_2^* + H_2 = 2 HCl^* \text{ or } HCl^* + HCl$$
$$HCl^* + Cl_2 = Cl_2^* + HCl....$$
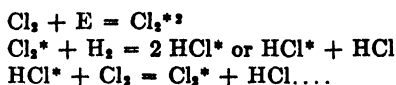
This would be an energy-chain instead of the former matter-chain. But the assumption of such an energy-chain involves a difficulty. That there are specific reactions between Cl and H_2 is evident, but here we must presume that the transfer of energy is specific too, and that the energy passes over from HCl^* only to Cl_2, and not to the molecules of the final product or to those of some foreign gas present.   Otherwise these molecules would be in competition with those of Cl_2 and ought to check the reaction.

This specificity of energy-transfer seemed at first unlikely, but now there is a good deal of proof that it really exists.   For instance, the fluorescence of mercury or sodium vapor excited by the absorption of their own light is extinguished by foreign gases which react quite specifically (3), and a quite similar phenomenon has been observed by Kistiakowski (4) in the photochemical decomposition of ozone.   These facts demand that there is a resonance between sender and receiver, and furthermore, that the spheres of action in these processes are much greater than those known from the kinetic theory of gases (5).   That would imply that the transferred energy is not a kinetic, but an internal energy, which corresponds exactly to the application of this energy to produce a chemical reaction.   This transfer of energy has been treated in the last months from the standpoint of the wave mechanics by Kallman and London (6) and may now be well understood by means of this theory.

The assumption of chain reactions has arisen from photo-

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[2] Cl_2^* means an excited molecule.   I proposed this interpretation in 1916 (Z. Elektrochem. 22, 53 (1916)) because my first interpretation, using a free electron as intermediate body, was proved to be impossible, and because the one proposed by Nernst was also thought to be impossible at that time because of an abnormally large heat of dissociation of the chlorine molecule, which rendered the reaction $Cl_2 + E = 2 Cl$ impossible for quanta of visible light.   Today we know that the heat of dissociation of the chlorine is much less, and that this reaction really occurs.

chemistry, but it may be used for reactions in the dark too.   Here the first example was in the formation of hydrogen bromide. Nearly twenty-five years ago Lind (7), while working with me in the laboratory of Ostwald, found that there was a very unusual law governing the velocity of this reaction.   At that time we did not find an explanation for the observed formula.   This explanation was obtained in 1919 by three independent authors,— Herzfeld (8), Polanyi (9) and Christiansen (10).   The chain assumed was:

1. $Br_2 = Br + Br$
2. $Br + H_2 = HBr + H$
3. $H + Br_2 = HBr + Br$, but also
4. $H + HBr = H_2 + Br$, and finally
5. $Br + Br = Br_2$

This was without doubt the first discussion of chain reactions occurring without light.   It may be mentioned that later we studied the influence of light upon this reaction too, and found that the combination of observations made in the light and in the dark has given important information concerning reaction 5, the first case in which it was possible to investigate the velocity of a reaction between atoms (11).

In the meantime a large number of such chain reactions has been studied in the dark as well as in the light.   The theory has also been generalized in two ways and has been applied to some special phenomena, giving very interesting results.

The first generalization was made by Christiansen and Kramers (12) to explain how the heat of activation in many gas reactions could be gained quickly enough by the molecules for them to react.   Here the authors have introduced the assumption that the energy is transferred from the products just formed to the reacting molecules by an energy-chain as described above, with the specificity of the energy-transfer which now has become well understood by means of the theory of wave mechanics.

A second generalization was made by Christiansen (13) and verified in some experimental investigations by Bäckström (14). These authors have advanced a theory of negative catalysis, using chain reactions for its explanation.

This theory arose also from photochemistry, especially from the reaction between hydrogen and chlorine. If we use the mechanism mentioned above as suggested by Nernst, or any other mechanism of that kind, it is not obvious why the reaction may come to an end, and why one quantum of absorbed light may not cause the formation of an infinite number of HCl molecules. Now we have known for a long time that oxygen checks the combination of hydrogen and chlorine in a remarkable manner— that it is a negative catalyst for this reaction. Discussing the law of the reaction velocity as governed by the concentrations of H_2, Cl_2 and O_2, one is led to the conclusion that there is a reaction between the hydrogen atom and the oxygen, which uses up the former and thus breaks off the chain (15). It is not quite clear what kind of reaction may occur here, but that this reaction terminates the chain has been shown quite clearly by Miss Cremer (16) in my institute by the fact that for one quantum absorbed one molecule of water is formed, independent of the length of the chain, i.e., independent of the number of HCl molecules formed.

Thus the negative catalyst breaks off the chain in this photo-chemical reaction. That many cases of negative catalysis may be easily explained in the same way has been predicted by Christiansen and has been proved in excellent investigations by Bäckström.

Let us now speak briefly of some further applications of the idea of chain reactions. Very interesting ones have been given recently by Haber and Bonhoeffer (17), also by Hinshelwood (18), Pease (19), Egerton (20), Semenoff (21) and other chemists. The reactions here in question are those occurring in the combustion of fuel gases,—hydrogen, hydrocarbons, and carbon monoxide. The German chemists have considered the reaction taking place in flames or explosions. With the aid of the spectroscope and our well-improved knowledge of spectra, and using our knowledge concerning the heats of dissociation of H_2, O_2, the C—C linkage and so on, they were able to find out what sort of intermediate molecules were formed between the starting substances and the final products. They observed the formation of OH, CH,

CC and other unstable materials. They were also able to answer the question as to how the chains are broken off—namely, by the loss of energy in the form of the radiations which give the special colors to the different flames or explosions.

The same reactions have been studied in many investigations from the standpoint of chemical kinetics. That is of course impossible when using flames or explosions, as it is necessary to work with lower temperatures in order to gain a moderate reaction velocity. In all these investigations it has been shown that the place where reaction occurred was not in the gas phase but on the walls of the vessels. It has been known for a long time that there is a narrow domain of a gas reaction of measurable velocity (22) between the temperatures of these wall-reactions and that of explosion. This small domain of temperature has now been studied by the above-mentioned authors, who have discovered that the combustions are chain reactions also, and that the chains are broken off by the walls. This result may be astonishing at first sight, especially since at slightly lower temperatures the reaction takes place on the walls exclusively; but it has been proved quite certainly, and it is after all not difficult to understand, since it is clear that the wall surface is able to take up the energy of the newly formed molecules as well as to adsorb unstable intermediate products, thus giving them occasion to combine with each other.

The idea that the combustions of gases are chain reactions, and that the chains are broken off on the walls or on other solid bodies present, has led to an explanation of the action of the antiknock materials used with easily combustible fuels in internal combustion motors. These antiknock compounds, vapors of lead tetraethyl or of pentacarbonyl of iron, added in small quantities to the hydrocarbon fuels before they are mixed with air and compressed, are decomposed by the high temperature produced by this compression, thus giving rise to a dust of metal or metallic oxide. This dust, present throughout the whole mass of the gases, breaks the chains of the combustion of the benzenes which would otherwise lead to a premature explosion of the mixture and thus to the knocking of the motor.

This is the theory of the action of antiknock compounds as given by Egerton. It may be said that it seems not quite certain whether the substances really cause a breaking-off of the chains on the surfaces of the dust particles. It may be that the "antiknocks" are negative catalysts in the sense suggested by Bäckström, and stop the combustion chain by being oxidized by the intermediate products of these chains. As far as I am aware no proper decision has yet been given as to their mode of action, but in both cases they act as inhibitors of combustion by breaking off the reaction chains.

There are some more applications and some further developments of the idea of chain reactions, but I think that this may be sufficient to give an account of the subject and to show how commonly chain reactions appear, at least in gaseous reactions.

It seems to me that chain reactions will become much more usual in proportion as gas reactions are studied more and more closely. It is not easy in every case to state that some reaction under investigation needs a chain for being completed. I said above that I was led to the assumption of the chains by the fact that in many photochemical reactions the number of reacting molecules was much greater than that of absorbed quanta. But at that time the Einstein law, which demands the identity of both of these numbers, was quite new, and seemed to be a somewhat bold postulate which one could either accept or reject, as was done at that time by other scientists.

But I found that the yield by the photochemical processes was not only too great, but was also dependent upon the concentration of the reacting substances, upon apparently foreign additions, and in many cases upon the temperature, and that these processes showed in many details the characteristic properties of purely chemical reactions. So I was led to treat them in the usual way for treating reactions in the dark,—to look for a law giving a relation between reaction velocity and concentration, and to try to find out in this way the nature of the intermediate products. This is not possible in all cases, but sometimes it has been very successful. Moreover, this is the way by which to decide in every

case whether a reaction is a simple one or whether it involves chains.

To illustrate this method, permit me to consider a special case which was investigated in an unusually successful manner a few months ago in my laboratory by Dr. Schumacher. The reaction was the decomposition of ozone, as catalyzed by chlorine, easily measurable in the dark at a temperature of 50°. The measurements indicated that there is a rather long period of induction, due certainly to the reaction itself and not to impurities, and that after this period of induction the velocity is given by

$$\frac{-\,d(O_3)}{dt} = k(Cl_2)^{\frac{1}{2}}\,(O_3)^{\frac{1}{2}}$$

We assumed the following series of reactions:

1. $Cl_2 + O_3 = ClO + ClO_2$
2. $ClO_2 + O_3 = ClO_3 + O_2$
3. $ClO_3 + O_3 = ClO_2 + 2\,O_2$
4. $ClO_3 + ClO_3 = Cl_2 + 3\,O_2$
5. $ClO + ClO = Cl_2 + O_2$

Calculating the velocity of each of these reactions as given by a constant $k_1 k_2 \ldots$, and the concentration of the reacting substances, we get a series of equations for the velocity of the change in concentration of each of the substances occurring in this scheme. So for ClO_2, for instance, we get

$$\frac{+\,d(ClO_2)}{dt} = k_1(Cl_2)\,(O_3) + k_3(ClO_3)\cdot(O_3) - k_2(ClO_2)\cdot(O_3)$$

If we assume that as soon as the induction period has been completed, the velocities of formation and of using up this intermediate product are equal to each other, for a period of time short in comparison with that of the main reaction, then we may put the whole $\dfrac{d(ClO_2)}{dt} = 0$. Doing the same with the analogous equations for the other intermediate products, we obtain equations which give the concentrations of the intermediate products

expressed by a function of the concentrations of the well-known measurable substances.

So we find in this case

$$(ClO_3) = \sqrt{\frac{k_1}{k_4} \cdot (Cl_2) \cdot (O_3)} \qquad ClO_2 = \frac{k_3}{k_2} \sqrt{\frac{k_1}{k_4} \cdot (Cl_2) \cdot (O_3)}$$

and for the velocity of decomposition of ozone,

$$-\frac{d(O_3)}{dt} = k_1 (Cl_2) \cdot (O_3) + k_2 \cdot (ClO_2) \cdot (O_3) + k_3 \cdot (ClO_3) \cdot (O_3).$$

Neglecting the first term as very small in comparison with the other ones,

$$-\frac{d(O_3)}{dt} \quad 2 k_3 \sqrt{\frac{k_1}{k_4} \cdot (Cl_2) \cdot (O_3) \cdot (O_3)}$$

This is the result as given by the experimental data. Of course, some simplifying assumptions were made in this calculation. In most cases justification is proved only by the fact that the equation calculated in this way agrees with that found by experiment. In this special case, where the induction period was very long, which implies that the constants of the intermediate reactions were measurably small, we were able to calculate all the single k's, thus verifying the validity of the assumptions made.

It is impossible to go into details with this reaction, which is in many respects especially interesting, but I hope to have shown, using this example, that the chain reactions which occur so frequently may be recognized with all desirable certainty by a careful measurement of the reaction velocity, even in those cases where it is impossible to know the number of the primary reacting molecules, as in photochemical processes.

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THE THERMAL AND PHOTOCHEMICAL SYNTHESIS OF PHOSGENE

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Carbon monoxide and chlorine are able to combine, forming phosgene, as well under the influence of light as at slightly higher temperatures with an easily measurable velocity. This reaction has occupied our attention since 1914. The reason for such a long series of investigations is that this is a real chameleon; the law of its reaction velocity changes from dark to light, and for the photochemical reaction from temperature to temperature. So I beg leave to give a very brief account of the observations we have made in this direction.

Let me begin with the reaction in the dark, which takes place with easily measurable velocity at 350–500°, and is accompanied by the reverse reaction, leading to an equilibrium. While this is of a perfectly normal kind given by
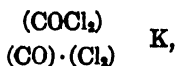
$$\frac{(COCl_2)}{(CO)\cdot(Cl_2)} \quad K,$$

the velocity with which it is established is not. This is given by

$$\frac{d(COCl)}{dt} = k_1\cdot(CO)\cdot(Cl_2)\cdot(Cl_2)^{\frac{1}{2}} - k_2\cdot(COCl_2)\cdot(Cl_2)^{\frac{1}{2}}$$

This equation expresses the fact that each of the two reverse reactions is catalyzed by chlorine atoms, present in low concentration in equilibrium with the chlorine molecules. An interpretation of the mechanism was given by Christiansen, who published a short paper on the decomposition of phosgene while Plaut and I were occupied with the investigation of both reactions. He proposed two series of intermediate reactions:

1. $Cl_2 \rightleftharpoons 2\,Cl$		1. $Cl_2 \rightleftharpoons 2\,Cl$
2. $Cl + CO \rightleftharpoons COCl$	or	2. $Cl_2 + Cl \rightleftharpoons Cl_3$
3. $COCl + Cl_2 \rightleftharpoons COCl_2 + Cl$		3. $CO + Cl_3 \rightleftharpoons COCl_2 + Cl$

225
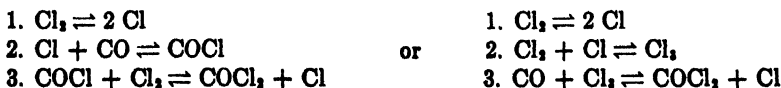
In both cases reaction 3 is slow; the equilibria 1 and 2 are continually established,—a view which may easily be accepted because there is only a very slow production or consumption of the components. It is impossible to decide between these two possibilities. On the other hand, Plaut and I were able to show that all results as derived from both these schemes agree even quantitatively with the facts.

Oxygen has no influence whatever on this reaction in the dark. But if one investigates the photochemical reaction at room temperature, one finds that oxygen is a very remarkable inhibitor, and that it is used up, forming carbonic acid, in a reaction which at even very moderate concentrations of oxygen preponderates to the exclusion of the formation of phosgene. A mixture of oxygen-free carbon monoxide and chlorine reacts with a velocity given by

$$+ \frac{d(COCl_2)}{dt} = k \cdot (I^*_{absorbed})^{\frac{1}{2}} \cdot (CO)^{\frac{1}{2}} \cdot (Cl_2)$$

* I = intensity of light.

the yield being of the order of magnitude of 3000 moles per Einstein, and changing of course with the concentration. If the absorbed energy is assumed to be proportional to the concentration of chlorine, a condition which is ordinarily permissible, this equation becomes

$$+ \frac{d(COCl_2)}{dt} = k' \cdot (CO)^{\frac{1}{2}} \cdot (Cl_2)^{\frac{3}{2}}$$

Even then it is not in agreement with that governing the reaction in the dark where (CO) appears in the first power, and therefore a different mechanism is necessary to explain this fact. The knowledge acquired in recent years that a reaction like the combination of chlorine atoms to form molecules is not a simple one has forced us to seek another type of reaction by which the chlorine atoms may disappear and thus explain the breaking of the reaction chains. This reaction is:

$$COCl + Cl = CO + Cl_2$$

and the whole scheme now adopted by us is:

1. $Cl_2 + E = 2\ Cl$
2. $CO + Cl = COCl$
3. $COCl = CO + Cl$ } equilibrium being established.
4. $CO + Cl_2 + Cl = COCl_2 + Cl$
5. $COCl + Cl = CO + Cl_2$

This series leads to the observed law of the reaction velocity and is in agreement with all facts. But it must be said, that reaction 4 is given only in a general form, because it is here, just as in the case of the reaction in the dark, impossible to decide which of the different possibilities included by it may be the best expression for the observed facts. These possibilities are:

$CO + Cl = COCl$ (Reactions 2 + 3)   or $Cl_2 + Cl = Cl_3$
$COCl + Cl_2 = COCl_2 + Cl$ $CO + Cl_3 = COCl_2 + Cl$
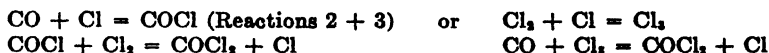
or even a three-body collision reaction, exactly like reaction 4 given above, which is not essentially different from the Cl_3 mechanism.

We are led somewhat further by observations of the photochemical reaction at higher temperatures in connection with measurements of the photosensitized formation of carbon dioxide. The latter takes place as soon as oxygen is present in the illuminated mixture of CO and Cl_2, and if the concentration of oxygen is higher than half that of chlorine, practically no more phosgene is formed, but only carbon dioxide. Its manner of formation must be through a chain reaction also, the yield being of the same order of magnitude as that of phosgene in the oxygen-free mixture.

The checking of the formation of phosgene and the formation of carbon dioxide may be explained on the assumption that reaction 4

$$CO + Cl_2 + Cl = COCl_2 + CO$$

is replaced by

$$COCl + O_2 = CO_2 + ClO$$

followed by

$$ClO + CO = CO_2 + Cl$$
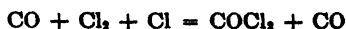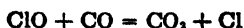
thus giving a chain.

The COCl was the substance which, reacting with Cl_2, terminated the chain in the oxygen-free reaction. If it is used up to a large extent it is no longer able to act in this way; the chains must be broken off by another reaction. The reaction $Cl + Cl = Cl_2$ is at least improbable; so the chlorine atoms must find another way to recombine, and that is by adsorption on the walls and a further recombination in the adsorbed state.

The consequence is that, for the photosensitized formation of carbon dioxide, the observed reaction velocity is no longer given by the square root of the absorbed energy, but by a power lying between the square root and the first power (to which the velocity of the diffusion of the atoms to the walls would be proportional) and changing with the form of the vessels, so that for larger ones the power is about one-half and for smaller ones practically one.

The power with which the absorbed energy enters into the law of the reaction velocity of the formation of phosgene changes in the same way if we change the temperature. Here several phenomena appear simultaneously: the photosensitized formation of carbonic acid ceases, together with the checking influence of oxygen; the power of the absorbed energy becomes exactly one, and this together with the fact that small amounts of impurity change the state of the walls and influence somewhat the reaction velocity. All these facts agree perfectly with the assumption that the equilibrium $CO + Cl \rightleftharpoons COCl$ is now changed so that only very low concentrations of COCl are available.

Since COCl is the substance leading to CO_2 formation, it is well understood that the formation of CO_2 ceases. But since COCl is also the substance which causes the consumption of Cl atoms, these now require another way of being consumed, i.e. by movement to the walls and by recombination on the walls. This is a diffusion process, and is therefore given by the first power of (Cl), thus leading to the first power of the absorbed energy in the equation for the velocity.

But this diffusion must depend upon the concentration of all gases and must be more rapid at low pressures. So we find the first power of the absorbed light already at somewhat lower temperature if the pressure is lower and if we go to pressures of a

few millimeters of mercury we can observe it even at room temperatures.

It should be possible, with the great number of measurements we have collected in a long series of investigations, to calculate in a somewhat quantitative manner all these rather complicated reactions. Perhaps that will happen in the near future, but today we are not able to do it in spite of our rich material. The greatest difficulty lies in the fact that the sensitized formation of carbon dioxide follows a law which we cannot yet interpret exactly. The velocity is given by

$$+ \frac{d(CO_2)}{dt} = k(I_{absorbed})^n (CO)^{\frac{1}{2}}$$

As long as the concentration of oxygen is not too low, it has not the slightest influence, while carbon monoxide occurs with its square root, and the absorbed energy with some power between the half and the first power as discussed above.

There is still a deep gap in our system. It is to be hoped that some one will have a good idea for filling it up and that then all these various reaction velocities may be reliably calculated, which will be of interest not only for the single question of the formation of phosgene but also for our general knowledge of chemical reactions.

ACTIVATION BY LIGHT AND BY COLLISIONS IN THERMAL EQUILIBRIUM

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The conception of activated molecules, now well established by the quantum theory, was first introduced by Arrhenius to explain the strong thermal acceleration of chemical reactions, and the success of this theory seems to prove positively that the activation of molecules is the first step of most reactions. But we still know very little about the mechanism of these activations.

A priori, the change in the energy of a molecule during an activation or a deactivation may be produced either by some interaction with another material system (molecule, atom, or electron), or by electromagnetic radiation. (In the first case the mechanism is usually called a *collision*; but as the distance of interaction is often much larger than the diameter of the molecules, it is sometimes better to use the word *induction*.)

The possibility of producing molecular activation or deactivation by means of radiation has been greatly emphasized by the quantum theory, whose fundamental relation determines the frequency of the light which can be connected with a given energy of activation. According to this theory, except in the single case of a metastable activated state, any activation can be produced by the absorption of a photon of the required frequency, and inversely, the return of the molecule to its normal state may occur by the spontaneous emission of a photon.

In a medium in thermal equilibrium, there must exist, according to the fundamental law of statistical mechanics, a well determined proportion of activated molecules of each substance present. But as all activated molecules are essentially unstable, such molecules can exist in a permanent state only if continually

new activations of ordinary molecules compensate the unavoidable deactivations of the activated molecules.

What is the origin of the energy required by these activations which occur in a medium in thermal equilibrium, for instance at room temperature, and are the first condition of any chemical reaction? Are they due to collisions between molecules, or to absorption of light borrowed from the thermal radiation? This question is very important for our knowledge of the mechanism of purely thermal reactions. (We shall not consider in this paper the thermal *chain* reactions in which most of the activations are due to the reaction itself and are not of thermal origin.)

It was at first admitted that the activations of molecules in the usual chemical reactions were due to collisions. But on this hypothesis it is difficult to explain the invariance of the rate of a gaseous monomolecular reaction when the pressure becomes very low. The only possible cause of activation is then the thermal radiation, and this is one of the reasons which led to the development of the so-called radiation hypothesis (Jean Perrin).

This radiation hypothesis had some theoretical success, but was proved to be certainly erroneous in the case of the few reactions which could be thoroughly studied. The experiments of Professor Farrington Daniels show that the thermal radiation is not the cause of the decomposition of nitrogen pentoxide. Moreover, very often there is not enough available energy in the thermal radiation to account for the reaction velocity observed. And, finally, though the coefficients of thermal acceleration of the chemical reactions which have been studied at room temperature correspond to active frequencies situated in the infra-red, no photochemical reactions have ever been observed in this region of the spectrum.

One might be inclined to conclude from these facts that the thermal radiation never takes any part in the activation of molecules at room temperature. However, this conclusion would also be erroneous. We shall see that the study of fluorescence, combined with an application of the principle of microscopic reversibility, proves that in certain cases the thermal activations of molecules are due to radiation. We shall find at the same time an

important characteristic of the mechanism of activation by collision (2) (3) (4).

Any fluorescence is due to the spontaneous deactivation with emission of light of molecules which have been activated by an external illumination, increasing greatly the intensity of the active radiation. Generally the number of emitted photons is smaller than the number of absorbed photons, and this fact proves that some of the molecules activated by absorption return to their normal state, without emission of light, by a mechanism producing kinetic energy and finally heat. The light efficiency, that is to say the ratio of the number of emitted photons to the number of absorbed photons, or, which is the same thing, of the number of deactivations by emission of light to the total number of deactivations, is usually less than one, and sometimes very small.

The probability of deactivation by emission is an internal probability practically independent of the external conditions. Therefore any variation of the fluorescence efficiency is due to a variation of the probability of kinetic deactivation. Such a variation is always observed when the concentration of the fluorescent substance is increased, the fluorescence efficiency becoming very small in highly concentrated solutions. This fact proves that the probability of kinetic deactivation of an activated molecule of the fluorescent substance is very much increased by the presence in its neighborhood of an ordinary molecule of the same kind. For instance, a molecule of fluorescein, activated by absorption of light in an aqueous solution, is practically unaffected by the presence of a great number of water molecules or by collisions with these molecules, since in a very dilute solution the fluorescence efficiency is nearly equal to one, which means that the deactivation is nearly always due to emission of light. But if in the neighborhood of this activated molecule there happen to be molecules of fluorescein in their normal state, it is very probable that a kinetic deactivation will occur.. It seemed very likely, by analogy with electromagnetic induction, that this sensitiveness to the presence of a molecule of the same kind, when other molecules were without any effect, was due to a resonance between the two molecules, and this hypothesis has been verified. In fact, the

diminution of the fluorescence efficiency is also produced by adding to the solution any substance having an absorption band close to that of the fluorescent substance, whatever the chemical differences between the two substances (1).

In short, the study of fluorescence, especially in liquid solution, gives a direct knowledge of three mechanisms of quantum transformations: activation by absorption of light; deactivation by emission of light; and kinetic deactivation by induction between two synchronous molecules, no such deactivation being generally possible between two different molecules having no resonance relation. This last mechanism is certainly connected with the mechanism of transfer of energy between two molecules in resonance, which has been explained by the wave mechanics.

Besides these mechanisms, only one other is well known—that is, the activation by collision between a molecule (or atom) and a free electron. The activation of a molecule by collision with another molecule, which is usually supposed to be possible, is on the contrary very incompletely known, and has been observed only in rather complicated phenomena such as the luminescence of positive rays.

It seems probable that any mechanism of molecular transformation might be exactly reversed, and Klein and Rosseland have shown the necessity of this possibility. The principle of microscopic reversibility, which is an extension of the second law of thermodynamics, compels us to admit that in a medium in thermal equilibrium, reverse mechanisms of activation and deactivation exactly balance one another. It is thus possible to infer from the observed existence of a mechanism of quantum transformation, that the reverse mechanism also exists, and we are sure that in thermal equilibrium both these mechanisms will have the same importance.

For instance, the inversion of the mechanism of activation by an electronic collision, or collision of the first kind, leads to a mechanism of deactivation by collision with a slow free electron, or collision of the second kind.

Similarly, we have seen that for certain fluorescent substances, a kinetic deactivation of the activated molecules may be produced

by the presence of a molecule in resonance, but not by the presence of other molecules. Therefore we are sure that an ordinary molecule of such a fluorescent substance may be activated by a collision with a molecule in resonance if there is sufficient available kinetic energy, but that it cannot be activated by collision with a molecule not in resonance with it, even if the required kinetic energy is available. For example, a molecule of fluorescein may be activated by a collision with another fluorescein molecule, but cannot be activated by collision with a water molecule, even if the kinetic energy available in both cases is the same.

We have thus found an important feature, which had not been suspected before, of the mechanism of activation by collisions. The available kinetic energy of two colliding molecules may produce an electronic activation of one of them, only if a resonance condition is satisfied.

The fact that a molecule of fluorescein in a dilute aqueous solution cannot be activated by the collisions of the surrounding water molecules, even if these collisions are sufficiently violent, makes it probable that if this molecule is activated it will be by absorption of radiation. A new application of the principle of microscopic reversibility proves that it is really so in this case, and, in general, gives for the first time a precise answer to the fundamental question of the relative importance of collisions and of radiation in the thermal activation of molecules.

Let us consider a certain substance at a given concentration and temperature,—for instance, one of the reagents in a chemical reaction going on under some well-defined conditions. We can measure the fluorescence efficiency corresponding to any state of activation of the molecules of this substance in the given conditions, by exposing the medium to an external beam of the light of the required frequency, having for this frequency a stronger intensity than the thermal radiation at the considered temperature. Let us suppose that this efficiency is one-third, i.e. among the molecules which have been activated by the external beam of light, one out of three will be deactivated by emission of light. The total probability of deactivation by emission of an activated molecule under given conditions must be independent of the cause of its

activation. Therefore, even if we cease to illuminate the medium from outside, we are sure that on an average one out of three molecules of the given substance in the specified activated state, whatever be the cause of their thermal activation, will be deactivated by emission of light, the two others being deactivated by kinetic processes. *Vice versa*, the statistical equilibrium of the system requires that the reverse mechanisms of activation should have the same probabilities, that is to say, that one out of three activations should be produced by absorption of light, provided by the thermal radiation. If it were not so, the substance considered would give to the thermal radiation more energy than it borrows from it, in opposition to the precise form of the second law of thermodynamics.

In general we see that: *The relative importance of radiation in the thermal activation of the molecules of a given substance is equal to the efficiency of the corresponding fluorescence under the given conditions.*

In a dilute aqueous solution of fluorescein in thermal equilibrium in a dark room, at the ordinary temperature, the few fluorescein molecules which will pass into the activated state corresponding to the absorption band in the visible spectrum, will receive their energy from the thermal radiation; they will be activated by absorption of light. And on the contrary, in a concentrated solution of the same substance, at the same temperature, nearly all the similar activations will be due to collisions, since then the fluorescence efficiency is very small; but in this last case, the activations will be due to collisions between two fluorescein molecules, and hardly ever to a collision with a water molecule.

If, in the chemical reactions which have been so far studied, the activations of molecules are due practically only to collisions and not to the thermal radiation, it may then be concluded that the efficiencies of the fluorescences which would correspond to these activations, are nearly zero. This is not very surprising, since the substances having a good fluorescence efficiency are indeed rather exceptional. Moreover, in the known reactions the energies of activation correspond to infra-red frequencies, and no fluorescence has ever been observed in this region of the spectrum. It seems

probable therefore, that in the infra-red the fluorescence efficiencies are usually very small, and this explains fully the general failure of the radiation hypothesis.   But if a substance having a strong infra-red fluorescence should be found, one might expect to observe with it some thermal chemical reactions for which the activations of molecules would be due to radiation.

SUMMARY

Deactivation of activated molecules by collision is very common, but deactivation by radiation is rather rare.   Deactivation by radiation has been studied through experiments on fluorescence, and it has been found that fluorescence can be quenched only by molecules which are in resonance with the activated molecules.

Applying the principle of microscopic reversibility, it may be concluded that the available energy of colliding molecules can produce electronic activation only if a condition of a resonance is satisfied.

The relative importance of radiation in the thermal activation of the molecule of a given substance is equal to the efficiency of the corresponding fluorescence under the given conditions.   In most chemical reactions which have been studied thus far fluorescence is negligible, and in these cases activation by radiation is relatively unimportant.

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THE THERMAL, ELECTRONIC AND PHOTOCHEMICAL DECOMPOSITIONS OF SOLID BODIES

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The photochemistry of solids has received relatively little attention, if one excepts numerous studies on the silver halides made in connection with the photographic process (1). A few quantitative studies of the rate of thermal decomposition of solids have been made, but, in general, little is known other than the products of the reactions. The effects of alpha and beta particles on solids have been observed (2), but the chemical effects of slow-moving electrons on solids have received little or no attention. Theoretical considerations underlying the various modes of decomposition are in a very rudimentary stage. It is the purpose of this article to bring together the existing data on these subjects and to point out certain theoretical difficulties and possibilities.

The reason for the sparsity of the data on the reactions of solids is not difficult to find. The following types of reaction seem to be evident: (*1*) those for which all of the products are gaseous; (*2*) those in which the solids, in decomposing, leave a solid residue. In the former case the products may have relatively little effect on the course of the reaction unless they are highly adsorbed by the remaining solid. It is true that the rate of reaction may seem to depend markedly on the method used for its determination, for the process of diffusion of the gaseous products through the crystal lattice may be an important factor. Fortunately, however, this effect may be neglected in many cases. Thus any method depending on the evolution of a gas would give

a true measure of the reaction rate only after a steady state had been reached.   In some cases the reaction may be limited to the surface molecules, and diffusion would not be of importance.   For

TABLE 1

Thermal decomposition of solids

SUBSTANCE	TEMPERATURE RANGE	E	CRYSTAL FORM	T_1 $(K = 0.01)$ ABSOLUTE	E/T_1	REFERENCE
	°C	cals./mole				
$FeCO_3$ (siderite)............	491–581	85,500	Trigonal	773	111	(14)
$CoCO_3$ (dry crystals).........	427–477	72,400[a]	Trigonal	713	102	(14)
		82,200[b]		738	111	
$ZnCO_3$ (zincspar)............	407–452	95,000	Trigonal			(14)
$PbCO_3$ (cerrussite)..........	320–350	69,600[c]	Rhombic	602	116	(14)(15)
Hg_2CO_3 (precipitated)[d]......						
Ag_2O[e] (dried crystals).......	327–353	31,000[f]	Cubic			(16)
Ag_2CO_3 (dry crystals).......	239–253	40,000[g]				(17)
Ag_2CO_3(amorphous)[h]........	227–268					(17) (18)
$H_2C_2O_4$ (anhydrous).........	130–170	52,100	Rhombic-bi-pyramidal	457	114	(19)
$MgCO_3$ (magnesite).........	416–487	110,000[i]	Rhombic			(20)
		204,000[k]				
		84,000[l]		756	111	
$CdCO_3$ (precipitated)........	376–410	50,000[m]	Trigonal			(21)
$KClO_3$ (crystals)............	100–255		Monoclinic			(22)

[a] Reaction: $2 CoCO_3 = CoCO_3 \cdot CoO + CO_2$.   [b] Reaction: $CoCO_3 \cdot CoO = 2 CoO + CO_2$.   [c] Reaction: $2 PbCO_3 = PbCO_3 \cdot PbO + CO_2$.   [d] Autocatalysis by Hg_2O.   Results not reproducible owing to effect of impurities and decomposition of catalyst.   [e] Autocatalysis by Ag.   Temperature Coefficient = 1.53.   [f] Calculated from data given by Lewis.   [g] Calculated by authors.   Data not constant.   Temperature Coefficient = 2.14.   [h] Decomposes to give unstable intermediate (oxycarbonate) which acts as autocatalyst.   [i] Calculated by authors for reaction $2 MgCO_3 = MgCO_3 \cdot MgO + CO_2$ for range 416–426°C.   [k] Calculated by authors for reaction $MgCO_3 \cdot MgO + 2 MgCO_3 = 3 MgO \cdot MgCO_3 + 2 CO_2$ for range 452–462°C.   [l] Calculated by authors for reaction $3 MgO \cdot MgCO_3 = 4 MgO + CO_2$ for range 470–487°C.   Only one of these three reactions has a specific reaction rate near 0.01.   [m] Calculated by authors.   An induction period is found.   Temperature coefficient = 2.02.

the second type of reaction, diffusion is often of importance and, in addition, the products of the reaction remain in intimate contact with the unreacted molecules, a fact which may lead to various secondary phenomena, such as autocatalysis.

These difficulties are present in all three classes of decomposition discussed in the present article. They are particularly difficult to overcome in studies of decomposition by radiation and by electron bombardment, for the amount of reaction is usually small and its detection difficult. Gas evolution methods are usually the most convenient to employ, but care is necessary because of adsorption.

THE THERMAL DECOMPOSITION OF SOLIDS

Table 1 gives a fairly complete list of the thermal decompositions of solids which have been studied from the standpoint of reaction rate. In nearly all, if not all, cases where the rate can be determined without ambiguity, the variation with temperature is satisfactorily given by the Arrhenius equation

$$K = A \ e^{-E/RT} \tag{1}$$

where K is the specific reaction rate, A is a constant, E the "heat of activation" or critical increment per gram-molecule, R the gas constant per gram-molecule per degree and T the absolute temperature. The reactions usually obey the equation for a unimolecular reaction

$$-dM/dt = K \ M \tag{2}$$

where M represents the amount of solid in convenient units and t is the time. In some cases, however, the rate is proportional to the surface of the solid instead of to its mass, and, in addition, the equation sometimes needs modification because of such phenomena as autocatalysis. An attempt has been made to point out facts of this nature in the footnotes to the table.

It has been shown for bimolecular gas reactions that E/T is nearly constant when various reactions are compared for identical values of K (3). Such a comparison is shown in table 1 for the decomposition of solids, the value $K = 0.01$ being chosen for the calculations. In many cases it was impossible to obtain the rate constants directly from the data given by the authors. The values of E/T show a surprising constancy, however. While the data on the decomposition of solid $KClO_3$ are not entirely satis-

factory, this substance almost certainly does not follow this generalization. It would be unwise, therefore, to make too broad a statement on the basis of the values given in the table, although it is possible that the relationship would be valid for those reactions for which catalytic effects are not important.

Theories of the mechanism of gaseous reactions have attained some success in the past few years in accounting for the rate of reaction on the basis of collisions (3, 4, 5, 6, 7, 8, 9). The complexity of the molecules has been considered, and the distribution of the energy among the various degrees of freedom has been treated with the aid of statistical mechanics. Thus far these theories may be said to be in a somewhat empirical stage, for the number of degrees of freedom which must be used in the calculations can not be obtained from any molecular model. Definite information as to the nature of the bond which must be activated is usually lacking. One may say, however, that it is possible to account for the magnitude of most homogeneous gas reactions by such calculations. Introduction of the ideas of pre-dissociation (10) (11) and further studies of the energy levels in complicated molecules will undoubtedly lead to more satisfactory results in the future.

Few attempts have been made to account for reaction rates in solution. Here it is difficult to treat the problem on the basis of collisions. One or two attempts have been made to account for the reaction rates of solids (12) (13).

For homogeneous gas reactions the order of magnitude of the "heat of activation" is from 10^4 to 10^5 calories per mole. In general, the heats of activation are not related to any frequencies in the absorption spectra of the reacting gases by the simple equation of the quantum theory $E = Nh\nu$, where N is Avogadro's number, h is Planck's constant expressed in the proper units and ν is the frequency. Numerous attempts to find such a relationship have been made as a result of the interest aroused by the radiation hypothesis (23). In most theories of gas reactions it is customary to assume that the relative kinetic energies of two molecules at impact, plus the internal energies of the two molecules, must exceed E/N in order to make reaction possible.

Reaction must occur during the interval between such an activating collision and a subsequent deactivating collision. During this interval the proper bond in the molecule must acquire a certain minimum amount of energy.

In the case of the thermal decomposition of solids it is difficult to arrive at any satisfactory formula for the possible number of activated bonds. If the solid is thought of as a system made up of a large number of harmonic oscillators, the fraction in any given quantum state would be given by the expression

$$P_1 = \frac{P_E \, e^{-E/kT}}{\Sigma \, P_j \, e^{-E_j/kT}} \tag{3}$$

where P_E is the *a priori* probability of the state under consideration and the summation in the denominator is to be taken over all possible states. If the *a priori* probabilities are all taken equal to unity, and there is an infinite succession of states close together, it is found that the fraction of oscillators with an energy greater than E_0 will be $e^{-E_0/RT}$ (E_0 in energy units per mole and R in the same energy units per mole per degree). If now an oscillator must possess an energy greater than E_0 as a prerequisite to decomposition, the specific reaction rate will be given by the equation

$$K = A \, e^{-E_0/RT} \tag{4}$$

This is identical with equation (1) in form. A would be a constant depending on the chance of reaction after activation. On the basis of this simple picture, therefore, A could not exceed the fraction of a group of molecules which could become activated in the proper time unit corresponding to K.

We find that the values of K for the thermal decomposition of anhydrous oxalic acid may be represented (19) by the equation

$$\log_{10} K = 22.859 - 11370/T \tag{5}$$

so that $E = 52100$ calories per mole. K is expressed in mins.$^{-1}$. Thus at a temperature of 443° K. (which is in the range of temperatures used in the investigation), $K_{443} = 1.56 \times 10^{-3}$, or if the unit of time is changed to seconds, $K^1_{443} = 2.6 \times 10^{-5}$. Therefore

$$e^{-52100/1.99 \times 443} = 2.16 \times 10^{-26}. \quad A = 1.20 \times 10^{21} \text{ secs.}^{-1} \tag{6}$$

The quota of active molecules must be restored 1.2×10^{21} times per second in order to maintain the rate of reaction. Without more specific knowledge of the solid state it is difficult to estimate whether this figure is at all reasonable. It is extremely probable that our treatment of the solid as a system of harmonic oscillators is entirely too simplified. Indeed, it is reasonable to suppose that the amplitude of oscillation may not have all values (except, perhaps, for oscillators on the surface). Suffice to say, however, that this value of A is larger than can be accounted for satisfactorily in homogeneous gas reactions.

Kassel (13) has considered the difficulties involved in interpreting the high rate of variation with temperature of the decomposition of calcium carbonate hexahydrate (13a), and has come to the conclusion that it is possible to explain the data satisfactorily by postulating a step-wise reaction. We shall show in the next few pages one method of treating the problem by introducing two steps, one of which is reversible. There is no very good reason for postulating such steps for the solids mentioned in table 1. It is conceivable, however, that any solid decomposition involves a rearrangement in space of some atom or groups of atoms, and that either reversion to the initial state or production of a new compound may result from this new configuration.

The recent work of Hume and Colvin (13a) on the decomposition of potassium oxalate hemihydrate indicates a very high temperature coefficient. It is doubtful whether either this reaction or the previously mentioned decomposition of calcium carbonate hexahydrate studied by Topley and Hume (12) can be accounted for entirely by a mechanism involving steps. The reaction takes place undoubtedly at an interface and the treatment given by these authors seems adequate.

The possibility must not be ignored, however, that some modified distribution law must be used, and that the quota of active molecules as calculated above is entirely wrong. Thus it might be possible to treat each unit in the crystal lattice as an entity, and obtain a value for the probability of its possessing a certain energy of oscillation. Upon ascribing a certain number of degrees of freedom to each unit, it would be possible to calculate

the chance that any one degree of freedom would possess the requisite energy for reaction. This treatment of the problem would be analogous to that used for gas reactions. Such a treatment, however, will scarcely account for the magnitude of A, and similar difficulties are encountered for the other solids given in table 1 for which the values of E/T_1 are about 111. Consequently, this line of attack will not be pursued further in this article, and we shall confine ourselves to the demonstration that most of the facts may be accounted for by assuming a step-wise reaction.

Let us assume the following mechanism

$$A = B; - dA/dt = k_1 A = + dB/dt$$
$$B = C; - dB/dt = k_2 B = + dC/dt$$
$$B = A; - dB/dt = k_3 B = + dA/dt$$
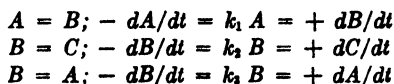
In the steady state we may assume that the amount of B will remain constant and we may write

$$B \quad \frac{k_1 A}{k_2 + k_3}$$

and the rate of the observed reaction will be

$$+ dC/dt = \frac{k_1 k_2 A}{k_2 + k_3}$$

Put

$$k_1 = a\, e^{- E_1/RT}; \ k_2 = b\, e^{- E_2/RT}; \ k_3 = c\, e^{- E_3/RT}$$

and

$$K \quad \frac{k_1 k_2}{k_2 + k_3}$$

It can now be shown that

$$\ln K = - \frac{E_1 + E_2 - E_3}{RT} - \ln (e^{- (E_3 - E_2)/RT} + c/b) + \ln a \qquad (7)$$

Referring to equation (5) we may put

$$E_1 + E_2 - E_3 = 52108 \tag{8}$$

and

$$a = 10^{22.859 - (E_2 - E_3)/2.3\,RT} + 10^{22.859}\,c/b \tag{9}$$

It now remains to test the equations for their applicability to the experimental data. If we put $E_1 = E_2 = 30054$ and $E_3 = 8000$, then c/b must have a small value in order to give a reasonable value to a. Let us assume that $c/b = 10^{-10}$. Then at 443°K., $a = 8.218 \times 10^{12}$. If $a = b$, we find that $c = 0.822 \times 10^3$. Therefore it can be shown that $k_1 = 1.294 \times 10^{-2} = k_2$, and $k_3 = 9.43 \times 10^{-2}$ if the time is taken in minutes. Thus the quota of molecules in the active state would only need to be restored 1.4×10^{11} times per second for the first and second reactions and only 10 to 100 times per second for the reverse reaction. If the reaction is purely on the surface and only one molecule in 10^5 is on the surface, the active quota would only need to be restored 1.4×10^{16} times per second for the forward reactions. There should not be a great deal of difficulty in accounting for this rate of activation.

At a temperature of 413°K., if c/b is still 10^{-10}, $k_1 = 9.76 \times 10^{-4} = k_2$, and $k_3 = 4.38 \times 10^{-2}$. The value of K calculated from these figures is 2.13×10^{-5}, which agrees with that obtained from equation (5). It would be impossible, from the experimental data, to detect the small variation with temperature necessitated by equation (9).

One other explanation is possible in the case of certain solids. Christiansen and Kramers (24) have postulated that a molecule on decomposing may transmit its excess energy to those immediately surrounding it, thereby producing a 'chain' reaction. This type of process might occur if the heat of reaction is small compared to the heat of activation. If the reaction is endothermic, the heat of activation divided by the heat of reaction would give approximately the number of molecules which might decompose in such a chain, providing the second molecule did not require the same heat of activation as the first. If the reaction is exothermic, an indefinitely large number of molecules might decompose in such a chain.

Such considerations as these may be of importance in some cases, but most of the solids mentioned in table 1 decompose with the absorption of energy, so that the explanation of the magnitude of the reaction rate must undoubtedly be found elsewhere.

Equation (1) has been derived by Tolman (25) in the form

$$\frac{d \ln K}{dT} = \frac{\bar{\bar{E}} - \bar{E}}{RT^2}$$

where $\bar{\bar{E}}$ is the average energy of the molecules which react and $\bar{E}$ is the average energy of all the molecules. As we have seen, most of the reactions of solids require a large difference between these energy terms. Hence some mechanism must be found which gives a larger quota of active molecules than can be obtained on any simple hypothesis.

Before concluding this section on the thermal decompositions of solid bodies, we must return to a fact which has been pointed out several years ago by Langmuir,—namely, that reactions are most apt to occur at an interface. The introduction of an interface into a solid body may lead to effects which have not been considered in this article. For example, the size of the interface and the character of its growth may suffer abnormal variations with temperature. Indeed, some work indicates that *perfect* crystals will not decompose unless they are first transformed either by scratching or by pressure. This would indicate that reproducibility should be difficult of attainment in studies of thermal decomposition. It can be shown, however, that one method of treating the problem of the interface mathematically leads to results identical in form with the step-wise reaction which we have postulated in the preceding paragraphs. In the case of oxalic acid, no interface between solid phases seems possible. The reaction probably takes place on the surface of the crystals.

The values of E/T may show an agreement which is of no theoretical significance. The fact that most of the solids considered are carbonates and that even oxalic acid decomposes to liberate carbon dioxide, may indicate, simply, a regularity in decompositions of this class. Further studies of other types of solid body will be necessary to decide this question definitely.

The large values of E/T indicate, however, that the fraction of active molecules must be small according to any simple theory of reactions taking place in one step which has been proposed.   If the reaction is restricted to an interface (which would limit the number of molecules capable of activations to a small fraction of the total), the A terms for the molecules in the zone of action would be much larger than the figures we have given and the difficulty in their explanation would be correspondingly greater.   It seems entirely possible, however, that the distribution law for solid bodies is not as yet fully understood and that the future may bring forth a satisfactory explanation along altogether different lines.   The new quantum mechanics leads us to believe that this may not be an impossible development in the very near future.

THE PHOTOCHEMICAL DECOMPOSITION OF SOLIDS

Little information on the photochemical decomposition of solids is recorded in the literature.   Several obvious difficulties are encountered in this type of work.

The determination of the quantum efficiency of a reaction of a solid would necessitate a measurement of the intensity of the incident as well as of the scattered radiation.   This latter involves great difficulties and probably has never been carried out with entirely satisfactory precision.   It may be estimated by means of a thermopile, which is moved into various positions with respect to the solid being irradiated.   The total amount of scattered radiation would be obtained by integrating over a complete sphere (26).

As a result of these considerations, measurements of the photochemical decompositions of solids usually are restricted to an approximate determination of the effective wave lengths and of the decomposition products.   We shall cite several photochemical reactions of solids to indicate the nature of the information available.

The rearrangement of o-nitrobenzaldehyde to o-nitrosobenzoic acid was first studied by Lobry de Bruyn (27), who found that a solid solution of the acid in the aldehyde was formed.   Bowen, Hartley and Scott (28) found that the quantum efficiency of this

reaction was about 0.5, neglecting scattered radiation. Padoa (29) investigated the reaction of single crystals in polarized light, and established that there were distinct differences in the speed of reaction according to the orientation of the crystal to the plane of polarization. Weigert and Brodmann (30) have studied this reaction in solution and find a quantum efficiency of about 0.5 independent of wave length. They find that the assumption of anisotropy of single molecules in solution offers a satisfactory explanation of their results.

Many examples of phototropy (31), or change in color upon irradiation, are known for solids. ·1-Keto-2,3,4-tetrachloronaphthalene, which is normally yellow, becomes green under the influence of visible radiation (32). The yellow hydrazones of aromatic aldehydes, $R_1 - CH = N - NH - R_2$, become rose, orange, purple or red brown (33). Many other examples could be given. The theory underlying these changes is not entirely satisfactory. It is probable that a single theory would not be adequate to explain all of the phenomena (34). Weigert (35) has discussed various aspects of photodichroism and photoanisotropism (35a).

The action of radiation on solid cinnamylidenemalonic acid, first investigated by Rüber (36), gives probably diphenyltetramethylenediethenyldicarboxylic acid under the influence of light. Bowen, Hartley and Scott (28) find the quantum efficiency to be about unity.

Renz (37) studied the action of sunlight on TlCl, both as a solid and in contact with various solutions. He found that the color became darker and that various compounds of thallium and chlorine were formed. He also investigated TiO_2, CeO_2 and Nb_2O_5 in a somewhat similar manner (38). Reaction was observed in all cases.

Many qualitative photochemical effects have been recorded, but an examination of the literature shows that few substances have been investigated from the standpoint both of thermal reaction rate and of photochemical reaction rate. Berthelot and Gaudechon (39) studied the photochemical decomposition of anhydrous oxalic acid and found that carbon dioxide, carbon

monoxide, hydrogen and traces of formic acid were formed.   They allowed the solid to reach a temperature of 95°C. due to the proximity of the quartz mercury arc lamp.   The decomposition was found to take place at wave lengths below 300 mμ.   Subsequent work (19) (40) has shown that the decomposition requires even shorter wave lengths, below 250 mμ, and that decrease in wave length leads to an increase in rate of decomposition. Whether this implies an increase in quantum efficiency or simply an increase in absorption was not ascertained.   The hydrate was found to decompose much more rapidly than the anhydrous material.   A period of induction was noted.   This was explained as due to the relatively slow diffusion of the decomposition products out of the crystal.   It may have been only an apparent effect due to the adsorption of the products by the surface of the crystals and the glass wall.   Support for this statement is found in the effect of long continued evacuation.   The length of the induction period was markedly increased thereby.

The theoretical interpretation of the wave length required for photochemical decomposition of oxalic acid is not certain.   We have already seen that some special postulate is probably needed to afford an explanation of the rate of thermal decomposition, and hence the apparent energy of activation would probably bear no relationship to the wave length of light necessary to cause photochemical decomposition.   Solutions of oxalic acid are decomposed by wave lengths somewhat longer than those necessary for the decomposition of the solid.

The action of the light may cause an increase in vibration quantum number of some of the bonds lying near the surface with the possibility that direct dissociation may result if the frequency is higher than that of the convergence limit.   The chance of such a large increase in vibration quantum number without change in electron level is usually small.   Or the phenomenon of pre-dissociation may be of importance (10) (11).   In this case the excitation to a higher level may be followed by a change in electronic level resulting in dissociation.

It may be of interest to inquire whether the radiation which causes decomposition might not produce dissociation directly

instead of activation. Since the reaction is probably to be represented by the equation

$$H_2C_2O_4 = HCO_2H + CO_2$$

the primary step may be the removal of a hydrogen atom. The heat of dissociation of the -O-H bond is not known, but it may be assumed to be similar to that required to dissociate an isolated OH radical into an oxygen and a hydrogen atom. The energy required for the latter may be obtained from the following heats of reaction:

(a)	$H_2 = 2 H$;	$\Delta H =$	102000 calories	(41)
(b)	$1/2 O_2 = O$;	$\Delta H =$	70000	(42)
(c)	$HOH = H_2 + 1/2 O_2$;	$\Delta H =$	57800	(43)
(e)	$H + OH = H_2O$;	$\Delta H = -112000$		(44)

Adding

$$OH = H + O; \Delta H = 117800 \qquad (44a)$$
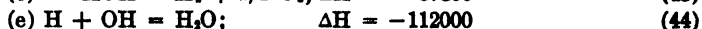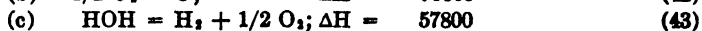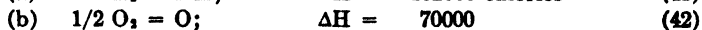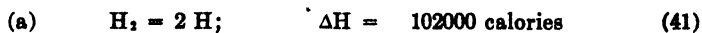
If the action of radiation were to remove a hydrogen atom without the production of an excited residue, a wave length of about $240\,m\mu$ could be calculated as necessary. The fact that this is in agreement with experiment may, of course, be an accident. It is obvious, however, that dissociation may be brought about by the radiation necessary to cause dissociation.

By the use of monochromatic light it has been shown that $KClO_3$ decomposes for wave lengths below about $280\ m\mu$ (45). The quantum efficiency is low. It is interesting to note that the wave length does not differ greatly from that required for oxalic acid, whereas the heat of activation for the thermal reaction is much lower, although its value is uncertain.

The photochemical decomposition of formic acid in the solid state has also been investigated (46). The quantum efficiency was about 1/50, neglecting scattered radiation. Only wave lengths below $300\ m\mu$ were effective.

In conclusion, we may state that although little information of a precise nature with regard to photochemical decompositions of solids is available, the facts warrant the adoption of principles similar to those used for other systems. Absorption by a solid

usually occurs in broad bands instead of in sharply defined lines. Nevertheless, dissociation and pre-dissociation may be thought of as occurring for surface molecules. No obvious relationship exists, in the few cases available for comparison, between the wave length of the radiation necessary for photochemical decomposition and the thermal heat of activation.

In this discussion mention of the silver halides has purposely been avoided, as they are discussed adequately in other reviews.

THE DECOMPOSITION OF SOLIDS BY ELECTRON BOMBARDMENT

The study of ionization and resonance potentials for gases has served to show the exactness of the relation

$$e\ V\ =\ h\nu \tag{10}$$

in such cases that an atom or molecule may be raised to some definite energy level by electron bombardment and may return to its normal state with the emission of radiation.

Direct dissociation of molecules into normal atoms is rarely, if ever, brought about by electron bombardment. The probability of increasing the rotational energy to the point of causing dissociation by such a process seems to be extremely small. Similarly, the chance of increasing the vibration level to such a point is negligible. However, dissociation may be brought about simultaneously with a change in electron level. The products of dissociation may be, in such a case, either a normal and an excited atom, or an ion and a normal atom.

It is now generally agreed that the dissociation of hydrogen into two normal atoms involves the absorption of energy corresponding to about 4.46 volts (41). Inelastic collisions between electrons and hydrogen molecules are not observed at this potential, however. Ionization of hydrogen molecules is produced at a potential of about 16 volts and the product is an H_2^+ ion (47). This ion may dissociate into an H^+ ion and a normal atom upon collision. Dissociation of the molecule into one normal atom and an atom in the 2 quantum state would require an energy corresponding to 14.63 volts. This process may be brought about by electron bombardment, as well as by radiation of wave length less than 84.94 mμ (48).

Somewhat similar relationships are obtained for other molecules. Therefore, if dissociation is to be brought about, either electron bombardment or radiation may be used. If a molecule is dissociated by radiation the following sets of products may be observed: (a) two normal atoms; (b) one normal and one excited atom; (c) two excited atoms; (d) one atomic ion and one neutral atom; (e) one atomic ion and one excited atom; (f) two atomic ions (one positive and the other negative). Not all molecules will exhibit these six different modes of dissociation. For each electron state of the molecule there will be a convergence frequency which will correspond to dissociation. It seems that dissociation by electron bombardment almost never occurs except when it accompanies a change in electron state. The first of these possibilities is, therefore, a rare occurrence when electrons suffer inelastic impact with molecules.

It can be seen from the foregoing that in some cases the relationship $eV = h\nu$ may enable one to predict what speed of electron will bring about chemical action, but that in other cases no such prediction could be made.

In addition to the foregoing possibilities, dissociation may result by the phenomenon of pre-dissociation. That is, when a molecule is excited to a higher electron level, its energy may exceed that necessary to produce dissociation in some other electron level. Under these conditions a change of electron level may occur and dissociation result. This phenomenon usually leads to a diffuseness of the lines in the absorption bands (10).

Theoretical studies of the solid state from the standpoint of energy levels are in a very elementary stage, but we may assume tentatively that conditions approximate those in gases. One should expect to be able to calculate the speed of electron which would cause reaction for some cases but not in others.

The kinetic energy of electron which will cause chemical reaction has been investigated for a few cases. Thus it is found that when the ionization potentials of nitrogen and hydrogen are exceeded, ammonia will be produced in a mixture of these two gases (49).

The electron bombardment of metals has been studied with

the following objects in view: (a) to ascertain the wave length of x-radiation emitted (50); (b) to ascertain under what conditions ultra-violet radiation is emitted (51); (c) to determine the nature of secondary electron emission (52); (d) to determine the law governing the scattering of electrons by crystals (53).

These studies have shown that the relationship $eV = h\nu$ holds within the limits of error for the excitation of x-radiation by electron bombardment. There is also some indication that ultra-violet radiation is given off when metals are bombarded by slow-moving electrons according to the same law. The emission of secondary electrons follows laws somewhat similar to those governing the photoelectric effect. The reflection of electrons from crystals follows laws somewhat similar to those governing the scattering of x-radiation. With certain corrections applied, it is found that the wave length of the electron is given by the de Broglie equation (54) $\lambda_e = h/mv$, where m is the mass of the electron and v its velocity.

The effects of alpha and beta particles on solids have been known qualitatively for many years (2). Thus glass becomes colored in the presence of radioactive materials. The alkali halides are also colored by their action. The change of white to red phosphorus has been investigated.

The effect of slow-moving electrons on non-conducting solids seems to have received little or no attention. There is considerable difficulty in interpreting the results in this case.

When a non-conducting solid is exposed to an electron stream, the surface of the solid should acquire a negative charge until such a point that the electrostatic repulsion prevents any further electrons from reaching it. If, however, there is a slight conduction along the surface, the charge should be gradually dissipated, and electrons should reach the surface with a kinetic energy dependent on the net effect of the various electric fields present.

The effect of electrons of varying kinetic energy has been studied for oxalic acid. The oxalic acid was placed on the pan of a sensitive balance in a vacuum. The pan of the balance was given a positive charge. A filament was used as a source of electrons and the range of velocity was limited by grids in the

usual manner.   With the arrangement of grids used, any positive ions formed in the gas between the grids would reach the surface of the solid and tend to neutralize the negative charge on it. If, then, the first few electrons which reach the solid cause decomposition leading to the production of some gas the process might continue.   Superimposed on the electronic decomposition there would be photochemical decomposition brought about by radiation produced in the gas phase.   This would, in effect, act as an amplifier of the effect being studied.

The results obtained indicated that when the kinetic energy of the electrons reaching the solid reached a value between 4.5 and 5.5 volts, decomposition resulted.   Five volts corresponds to a wave length of about 250 mμ, so that the relationship $eV = h\nu$ would seem to be verified.   The number of electrons per molecule of solid decomposing was about 10^{-3}.   These results are open to question for the following reasons: (a) the charge on the solid may render the velocity of the electrons uncertain; (b) oxalic acid does not have a negligible vapor pressure at room temperature (55), so that in spite of the removal of the vapor by liquid air, some photochemical decomposition may have resulted, owing to ionization and resonance in the vapor phase; (c) thermal radiation from the filament may cause a slight amount of decomposition. This error should be negligible.

Similar experiments with potassium chlorate (45) indicate that slight decomposition is produced by electrons at 22 volts.   An ionization gauge of high sensitivity was used to detect reaction by measuring the pressure increase.   Consideration of the probable adsorption of oxygen in the liquid air trap makes it seem probable that decomposition would not have been observed unless 10 to 100 molecules had decomposed per electron.   Since the reaction is decidedly exothermic such a figure might not be surprising. We may say tentatively, that the relationship $eV = h\nu$ does not permit of prediction of the proper speed of electron to cause decomposition in this case.

SUMMARY AND CONCLUSIONS

It is found that many solids decompose thermally, and that the heats of activation are rather high.   The probability that the

expression $e^{-E/RT}$ represents the fraction of molecules in the active state has been discussed. It is concluded that the magnitude of the reaction rates may be accounted for by postulating reaction in steps. It is possible, however, that when more is known of the solid state, some mechanism may be available for providing activation rapidly enough.

The photochemical decomposition of solids may be considered in terms analogous to those used for gases. The wave length necessary to produce decomposition may not be calculated from the heat of activation for the thermal reaction.

The various aspects of the electron bombardment of solids have been discussed. It is found that the electron energies necessary to produce decomposition may not be calculated in some cases from the wave length of radiation which causes the same process. It is shown that the decomposition of oxalic acid by electron bombardment may be in agreement with the relationship $eV = h\nu$, but that lack of agreement is found for $KClO_3$.

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HEATS OF ADSORPTION AND THEIR BEARING ON THE PROBLEM OF ADSORPTION

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I. INTRODUCTION

The process of adsorption involves the generation of heat. If no external work is done during the adsorption, the liberated heat is equal to the product of the quantity adsorbed by the difference in the energy of the gas before and after adsorption (Hückel). If we reduce all values to those for one gram of adsorbent, the irreversible integral heat of adsorption is

$$q = a \ (E - \epsilon),$$

in which a represents the number of gram-molecules of gas per gram of adsorbent, E the energy per gram-molecule of gas before adsorption and ϵ the same after adsorption.

If a is increased by da, without any external work, the irreversible differential heat of adsorption per gram-mol is

$$q_d = E - \epsilon - a \frac{d\epsilon}{da}$$

for an ideal gas.

If the adsorption takes place isothermally while the total number of molecules is kept constant, e.g. by moving a piston, then work is done. This work is $p \ dV$ (dV is the volume of the gas which disappears), consequently $p \frac{RT}{p} \ da$. Per gram-mol of gas adsorbed the work consequently is RT and

$$q_{\text{isotherm}} = q_d + RT.$$

An isobar heat of adsorption is possible, whereby a and T are varied at a constant p, as well as an isostere heat of adsorption

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whereby a remains constant, but a new p against T equilibrium is put in. Freundlich compares this heat with heat of evaporation, because during evaporation the composition of the phases also remains unchanged and only p and T are altered. This comparison however is confusing, as Williams has already pointed out. For if we bring the system water:water-vapor to a higher temperature, but in such a way that absolutely no water evaporates or condenses (hence by reducing the total volume), the heat supplied has nothing to do with the heat of evaporation, but only with the specific heat of water and water-vapor and with a small amount of heat of compression. In the case of the isostere heat of adsorption the same is also true, for this is a specific heat. The heat of adsorption which has been determined experimentally is not exactly defined theoretically. It lies between q_d and q_{isotherm}, as it does not take place quite without external work, but it cannot be decided whether, and to what extent, this work is transferred to the calorimeter as heat. When adsorption of a vapor takes place until the adsorbent is in equilibrium with the saturated pressure, we get the same condition which results when the evacuated adsorbent is directly wetted by the liquid in question. Furthermore, this wetting gives a heat effect smaller than the heat of adsorption, because the difference between these two, the heat of condensation, is always positive. The heat of wetting is usually determined by wetting a known amount of solid with an excess of liquid. This heat of wetting is hardly reproducible.

II. EXPERIMENTAL DATA ON HEATS OF ADSORPTION

We have published in the International Critical Tables, Vol. V, pp. 139–143, all reliable data on heats of adsorption determined experimentally, in so far as they were published before the year 1927. At the end of this section we shall give a summary of the more recent experiments.

The oldest quantitative experiments on the heat of adsorption are those of Favre, dating from 1874. Using a mercury-calorimeter he determined the integral heat evolved by the adsorption of different gases on charcoal at room temperature and at a

pressure of one atmosphere. He used six types of charcoal, made from various kinds of wood, but the results obtained with a single kind of charcoal differ from one another about as much as those obtained with various sorts of charcoal. Also, the quantity of gas adsorbed by the charcoal at one atmosphere varies considerably in control experiments, but the quotient of heat and quantity of gas adsorbed, i.e. the mean liberated heat per cubic centimeter, is approximately constant.

Nine years later, in 1883, Chappuis published his measurements on the heat of adsorption of various gases on charcoal (made of wood of *Evonymus europaeus*) and on meerschaum. The method applied by him has been used by most investigators since then.
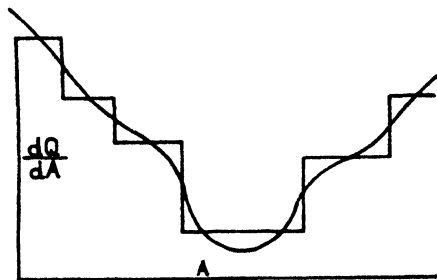
FIG. 1. DIFFERENTIAL HEAT OF ADSORPTION

To a weighed amount of evacuated charcoal in the ice-calorimeter, gas is admitted in known small portions. Before every admission and after adjustment of the equilibrium the pressure is measured, and since the volume of the apparatus is known, the quantity adsorbed per gram of charcoal can be calculated; we call this ΔA and express A in normal cubic centimeters (under normal conditions of temperature and pressure).[1] From the displacement of the thread of mercury the heat developed by the adsorption of ΔA is known; let this be ΔQ. We can now draw graphically $\dfrac{\Delta Q}{\Delta A}$ (the evolved heat per cubic centimeter of gas

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[1] When the adsorbed gas is expressed in gram-mols we write a, when expressed in normal cubic centimeters we write A. In the case of vapors condensing at normal temperature and pressure, 1 normal cubic centimeter (ncc.) means 1/22,400 gram-molecule.

adsorbed) against A, and we then get a stepped figure (figure 1). From this the real dependence of the heat of adsorption on A can be estimated by drawing a smooth curve, in such a way that each time the surface between that curve, the abscissa and two lines parallel to the ordinate, is equal to the surface enclosed by the steps.
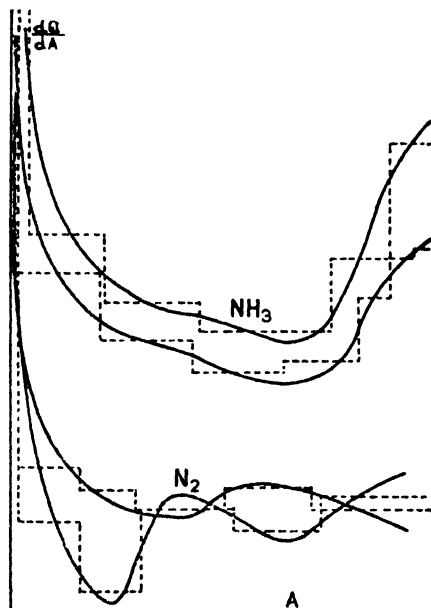
FIG. 2. CONTROL DETERMINATIONS OF N_2 AND NH_3 ON CHARCOAL AT 0°C. (TITOFF)

The scale of A and the value of $\dfrac{dQ}{dA}$ of the abscissa are different for the two gases.

Chappuis, in general, took too large volumes of gas (the steps were therefore too broad) to conclude much from his measurements except that $\dfrac{\Delta Q}{\Delta A}$ does not decrease in all cases with increasing A, as was expected, but that the curve sometimes shows a minimum, for instance with NH_3 on charcoal. This was evident in Titoff's experiments of 1910; he determined very accurately the heats of adsorption of N_2, CO_2 and NH_3 on cocoanut charcoal.

The results of his control determinations with NH_3 and N_2 are shown in figure 2. From this we get an impression of the reproducibility of these experiments, which is not great even when one works very accurately. This method of graphical representation reveals experimental errors in a very sensitive way; we deal here always with quotients of two values, of which one (ΔQ) is especially subject to a considerable percentage error.

Many investigators therefore draw their results only in the form of a Q against A curve, or express them in an exponential formula of the type $Q = m A^n$ (in which m and n are constants). The influence of experimental errors is then much smaller, but
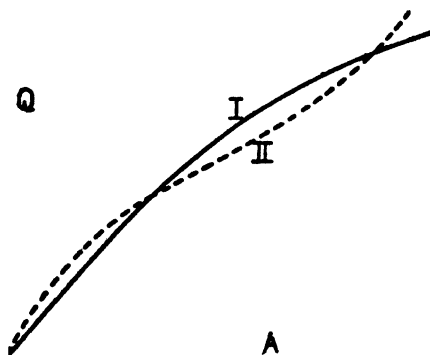
FIG. 3. I—CURVE WHICH CAN BE REPRESENTED BY AN EXPONENTIAL EQUATION; II—REAL CURVE

the curve no longer reveals much. Moreover, in those cases in which the $\dfrac{dQ}{dA}$ curve has an extremum, the Q against A curve must have an inflexion-point which cannot be expressed by the exponential formula. That in some cases the latter does not seem so unsatisfactory is due to the fact that the deviations between the real curve and that of the formula are distributed on both sides and are therefore unjustly attributed to experimental errors (figure 3). Therefore $\dfrac{\Delta Q}{\Delta A}$ is always given in the following tables.

For the present we must content ourselves with knowing

the approximate course of the $\dfrac{dQ}{dA}$ against A curve, without being able to indicate exactly where there is, for instance, a minimum. This is still more evident when we compare the results of different authors investigating the same system, such as ether on charcoal. This system has been examined by Lamb and Coolidge, by Keyes and Marshall at 0°C. and by Pearce and Lloyd McKinley at 25°C. (see table 2). Considering that they worked with charcoals of different structures and of very different adsorbing capacities, the agreement between their results is certainly satisfying (figure 4). In all cases the curve first falls steeply, then runs about horizontally, falls again and rises a little at the end. Whether
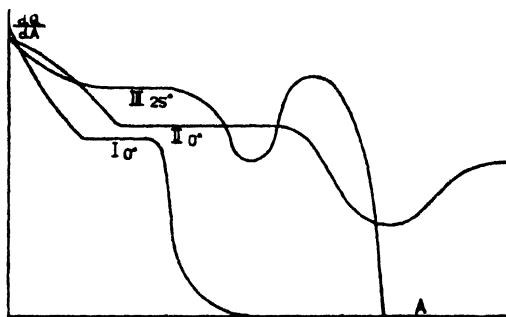
FIG. 4. ETHER ON CHARCOAL
I, Keyes: II, Lamb and Coolidge; III, Pearce and Lloyd McKinley

the horizontal part is real, in that $\dfrac{dQ}{dA}$ indeed remains constant during some distance, or whether the real course shows perhaps a minimum and a maximum, cannot be decided for the present.

The latter course was found by Williams (85) for SO_2 on blood charcoal at −20°C. in an investigation which he continued until the saturation pressure of SO_2 was reached; the curve then ends at the heat of condensation (figure 5). Many vapors of organic liquids show a similar behavior (see table 2 (Pearce and Lloyd McKinley) and table 3 (Gregg)). Also for CO_2 on charcoal Gregg (31) found that the curve after a flat minimum begins to rise again (see table 3); this rise however lies at a higher pressure

than is usually investigated. Going further still, the curve is due to bend again, as the heat of condensation of CO_2 (0.11 calorie per normal cubic centimeter) is much lower.

That the heat of adsorption is greatest for the gas first adsorbed is only relatively true. There are systems, where $\frac{dQ}{dA}$ rises first and does not decrease until afterwards. Cases where this was clearly found to be true are the following: O_2 on charcoal (Garner and McKie, see table 6); H_2 on nickel containing thorium oxide (Fryling, see also Beebe and Taylor); H_2O on charcoal (Keyes and Marshall); while Gregg observed with N_2 and N_2O on char-
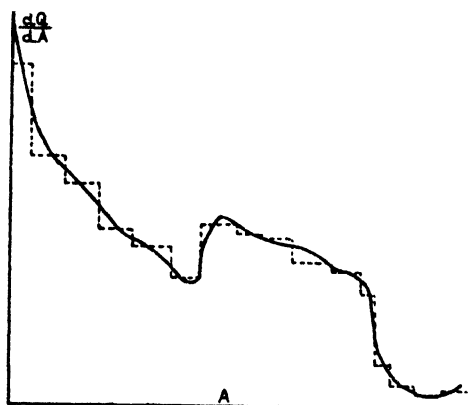
FIG. 5. SO_2 ON BLOOD CHARCOAL AT $-10°C$.

coal that the first $\frac{\Delta Q}{\Delta A}$ lies sometimes lower than the next one, but this difference is comparatively small. The charcoal used by Gregg was activated with N_2 containing 0.5 per cent O_2.

The investigations of Garner and McKie and of Fryling are very important owing to the small concentrations used, and owing to the great differences in the heats of adsorption found. With Garner the first value of $\frac{\Delta Q}{\Delta A}$ is one-fourteenth of the maximum. The maximum values for the heat of adsorption of O_2 on various kinds of charcoal, examined by Garner, are almost equal

(also nearly equal to the value found by Keyes and Marshall), but the concentration of the maximum differs.

Curves with a maximum are also found for H_2 with copper catalysts by Kistiakowsky, Flosdorf and Taylor, who however published only curves, without numerical data. They found that with an active catalyst H_2 gives a curve with a maximum at a low concentration (figure 6, curve 1). If the catalyst has lost much of its activity by being heated for a long time at 250–300°C., the $\dfrac{dQ}{dA}$ curve has a much flatter form (curve 2); when the catalyst is poisoned by O_2, we get curve 3. For CO with the same catalysts a curve was found which first descends and then shows a mini-
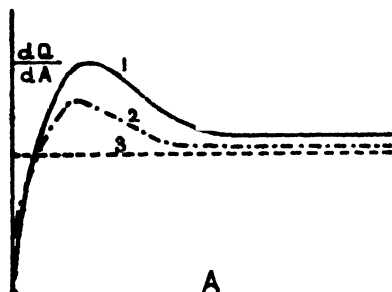
FIG. 6. H_2 ON COPPER CATALYSTS
1—catalyst very active; 2—catalyst less active; 3—catalyst poisoned

mum at the same quantity of adsorbed gas which gives a maximum in the H_2 curve.

If we compare the values for one gas on various kinds of charcoal, we see that in most cases only the initial values of $\dfrac{\Delta Q}{\Delta A}$ are strongly divergent. As a matter of fact, with each adsorbent the influence of its previous treatment is important for the first cubic centimeters of gas, but becomes less and less as more gas is adsorbed. If we calculate $\dfrac{\Delta Q}{\Delta A}$ over a large range of A (for instance, from $p = 0$ to $p = 760$ mm. Hg) the original condition of the adsorbent can be only faintly traced (see table 1.)

When on the contrary we take the values for the first volumes

of gas admitted, there is a great difference.   For charcoal, out-
gassed at 600°C., Magnus and Kälberer have found 0.558 calorie
(see table 4) for the initial $\frac{\Delta Q}{\Delta A}$; for the same charcoal, outgassed
at 100°C., the value is 0.378 calorie.   Foresti (24) has deter-
mined the influence of the temperature of outgassing on the
heat of adsorption of H_2 on nickel.   The quotient of Q and A
(between 0 and 760 mm. Hg.) decreases considerably at a lower
temperature of evacuation.

Lamb and Coolidge have worked with two sorts of cocoanut
charcoal of a different activity.   The activation was done by
treating the charcoal with steam during some hours at a high

TABLE 1

Adsorption of carbon dioxide on charcoal

INVESTIGATOR	TEMPERA- TURE OF OUT- GASSING	$\frac{\Delta Q}{\Delta A}$ 0 to 76 cm.	KIND OF CHARCOAL
Keyes and Marshall	900°C.	0.313	French gasmask
Magnus and Kälberer	600°C.	0.313	Wood charcoal
Favre	?	±0.311	Various kinds
Gregg (31)	400°C.	0.311	Birchwood
Titoff	400°C.	0.311	Cocoanut charcoal
Magnus and Kalberer	100°C.	0.308	Wood charcoal
Chappuis...	?	0.304	*Evonymus europaeus*

temperature.   As a measure of the activity the "service time"
was measured, i.e. the time during which the charcoal can retain
all the poisonous gas, for instance chloropicrin, out of a mixture
of air and poisonous gas of constant concentration and rate of
flow.   The relation between this service time (which is of great
interest for charcoal for gasmasks, and about which many investi-
gations have been made) and the further properties of a charcoal
is not simple.   On the other hand, the investigation of Lamb and
Coolidge shows that the heat of adsorption is almost independent
of a change in the activity.

The influence of the temperature on the heat of adsorption has
been examined by Gregg (31) (see table 3), who measured SO_2
and N_2O on charcoal at many temperatures.   Also by comparing

the results of Dewar, who worked at $-183°C$., with those of Titoff and Whitehouse, and by comparing the measurements of Lamb and Coolidge at $0°C$. with those of Pearce and Lloyd McKinley (see table 2), who worked at $25°C$., some knowledge may be obtained concerning the influence of the temperature on the heat of adsorption.

In these cases it appeared that the heat effect was greater at a higher temperature. Recent investigations however lead to another result. Magnus and Giebenhain (table 4) find for CO_2 on charcoal and on SiO_2 a smaller integral heat of adsorption at $25°C$. than at $0°C$. Kälberer and Schuster (table 7), who measured
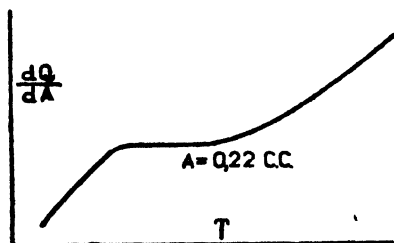
FIG. 7. CHANGE OF THE HEAT OF ADSORPTION OF O_2 ON CHARCOAL WITH T AT CONSTANT A

the heat of adsorption of CO_2 on SiO_2 at $0°C$. and at $75°C$., find that for high concentrations $\frac{dQ}{dA}$ is greater at $0°C$., but they suppose that at a small A the opposite will be true.

For O_2 on charcoal Garner and McKie give a graph for the relation between $\frac{dQ}{dA}$ at constant concentration and temperature (figure 7). There is a range of temperature between $100°C$. and $200°C$. where the heat of adsorption remains constant; afterwards it rises again. Whether this is a special case, or whether it is a general phenomenon, is unknown. It is true that we often find in the literature the opinion that the temperature coefficient of the heat of adsorption should be very small, although this has never been proved.

The investigation by Keyes and Marshall of H_2O on charcoal is remarkable not only because of the shape of the curve found, but

also because the heat of adsorption (from 0.38 to 0.47 calorie) is smaller here than the heat of condensation, which amounts to 0.487 calorie per normal cubic centimeter. Usually the heat of adsorption is much greater, especially with vapors of organic substances on charcoal. For benzene the heat of evaporation is 0.348 calorie at 0°C., the heat of sublimation 0.476 calorie, and the heat of adsorption on charcoal more than 0.6 calorie per normal cubic centimeter. Consequently the heat of wetting of charcoal with benzene and other organic liquids must be positive, and that of charcoal with water negative. Gaudechon, working with benzene on sugar charcoal (dried at 100°C.) found a heat of wetting of 4.2 calories per gram of charcoal. Gurvic obtained on bone black 11.1 calories per gram. The charcoal used by Lamb and Coolidge, which had been evacuated at 350°C., adsorbs more than 100 normal cubic centimeters of benzene per gram on saturation at 0°C.; this should give therefore a heat of wetting of at least 25 calories.

For carbon disulfide the relation is analogous: Gaudechon finds 4.0 calories per gram of sugar charcoal; Gurvic finds 13.9 calories per gram of bone black, and at least $150 \times (0.505$ calories -0.305 calories$) = 30$ calories per gram is calculated. (We assume that 150 normal cubic centimeters is adsorbed at 0°C. and that the heat of condensation of CS_2 is 0.305 calories per normal cubic centimeter.)[2]

Hence it is clear that unless the same charcoal, evacuated at the same temperature, is used, such comparisons are not justified. For H_2O this is still more important; here Gaudechon finds 3.9 calories per gram of animal charcoal, Gurvic and also Harkins and Ewing find 18.5 calories per gram of bone charcoal and Katz finds 20.9 calories per gram of animal charcoal. With the exception of Gaudechon, all used charcoal with a large ash content (investigations with ash-free charcoal have not been made); Keyes made his charcoal free of ash save for 0.36 per cent. The influence of this, especially for H_2O adsorption, will be discussed later on.

[2] In recent investigations Bartell and Ying Fu publish a heat of wetting of 32.7 calories for benzene on charcoal and of 31.2 calories for carbon disulfide on charcoal.

All of the experiments with water on charcoal have given a positive heat effect; on sand, however, such is not the case. Jungk, Schwalbe, Bellati and others observed a lowering of temperature when well-dried river sand at 0°C. was wetted by water. The effect was always small and has never been determined quantitatively.

In an investigation by Parks, various sorts of SiO_2 of very different specific surfaces were wetted by H_2O. Parks was able to determine the diameter of the particles microscopically and to calculate the surface from this. He found that the heat liberated per square centimeter of surface was constant.

This explains at the same time, why the values obtained with various sorts of charcoal vary so widely—namely, because the inner surfaces of charcoals are so different.

The values, expressed in joules, of the heats of adsorption of the following substances are given in the International Critical Tables, Vol. V, pp. 139–143: charcoal as adsorbent—air, NH_3, A, C_6H_6, CO_2, CS_2, CO, CCl_4, Cl_2, $CHCl_3$, CCl_3NO_2, C_2H_5OH, C_2H_5Br, C_2H_5Cl, $(C_2H_5)_2O$, $HCOOC_2H_5$, C_2H_5I, H_2, HBr, HCl, HI, CH_4, CH_3OH, CH_3Cl, N_2, N_2O_3, O_2, SO_2, H_2O; SiO_2 as adsorbent—SO_2, H_2O; meerschaum as adsorbent—NH_3, CH_3OH, SO_2; Ni as adsorbent—CO_2, C_2H_6, C_2H_4, H_2; Cu as adsorbent—H_2; Pt as adsorbent—H_2, O_2. In tables 2 to 8 the values of the heats of adsorption are expressed in calories. Unless otherwise indicated, A is given in normal cubic centimeters. In the case of vapors condensing at normal temperature and pressure, 1 normal cubic centimeter (1 ncc.) means 1/22,400 gram-molecule. In the following alphabetical summary of the substances whose heats of adsorption are given in tables 2 to 8, the figures refer to the tables; the letters to the sections of the tables:

Charcoal as adsorbent

$(CH_3)_2CO$	C_2H_2	C_4H_8	CO_2	CS_2	CCl_4	$CHCl_3$	C_2H_6
2A	3A	2I	3D, 4A	2C	2E	2D	3C

C_2H_5Cl	C_2H_4	$(C_2H_5)_2O$	CH_3OH	C_3H_7Cl	N_2O	O_2	SO_2
2F	3B	2B	2H	2G	3E, 3F	5, 6A, 6B	3G, 3H

Other adsorbents

ADSORBENT	GAS					
	NH$_3$	A	CO$_2$	C$_2$H$_4$	H$_2$	N$_2$
SiO$_2$......................		7A	4B, 7D	7C		7B
Ni........................	8B				8B	
Cu........................	8A					
Fe..............................	8C					

TABLE 2

Heats of adsorption of organic vapors on cocoanut charcoal outgassed at 550°C.

PEARCE AND LLOYD MC KINLEY

p mm. from to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories	p mm. from to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
A. Acetone at 25°C.				**F. Ethyl chloride at 25°C.**			
0.0 – —	6.44	4.59	0.713	0.0 – —	7.00	3.82	0.546
— – —	15 90	11.21	0.700	— – —	23.37	12.47	0.528
— – —	29.45	19.36	0.601	— – —	40.39	20.52	0.491
— – 1.1	47.93	30.89	0.624	— – 14.55	63.78	31.82	0.470
1.1 – 2.45	64.76	42.90	0.714	14.55– 43.0	81.80	40.64	0.489
2.45– 40.85	99.87	62.52	0.559	43.0 –223.4	99.49	50.76	0.572
40.85–130.24	109.28	67.87	0.569	**G. Propylchloride at 25°C.**			
B. Ethyl ether at 25°C.				0.0 – —	8.39	6.48	0.772
				— – —	24.65	17.36	0.669
0.0 – —	8.39	6.36	0.758	— – 1.90	37.99	26.10	0.655
— – —	24.26	17.85	0.724	1.90– 5.90	54.54	36 51	0.629
— – —	39.81	28.81	0.705	5.90– 55.09	66.10	43.16	0.575
— – —	55.36	38.29	0.610	55.09–349.5	77.98	48.83	0.477
— – 41.85	66.99	46.71	0.724	**H. Methylalcohol at 25°C.**			
41.85–367.2	78.00	50.30	[0.326]	0.0 – —	8.96	6 72	0.750
C. Carbon disulfide at 25°C.				— – —	23.42	15.41	0.601
				— – —	33.13	20.39	0.513
0.0 – —	7.50	4.82	0.643	— – —	48.41	28.73	0.546
— – —	20.56	12.35	0.577	— – 4.85	74.65	43.44	0.561
— – —	31.78	18.17	0.519	4.85– 7.25	98.80	56.01	0.520
— – —	42.27	23.11	0.471	7.25– 14.30	126.41	73.47	0.632
— – —	62.70	33.64	0.515	14.30– 41.35	158.03	88.09	0.462
— – 6.3	84.29	44.41	0.499	**I. Benzene at 25°C.**			
6.3 – 17.4	106.08	55.06	0.489	0.0 – —	14.00	10.67	0.762
17.4 –211.4	130.45	65.88	0.444	— – —	27.30	19.63	0.674
D. Chloroform at 25°C.				— – —	46.52	32.30	0.659
				— – —	66.39	45.09	0.644
0.0 – —	9.40	6.76	0.719	— – —	79.22	52.99	0.616
— – —	20.83	14.45	0.673	— – 60.65	87.29	58.00	0.621
— – —	34.84	23.24	0.627				
— – —	56.41	35.84	0.584				
— – 4.65	74.80	46.59	0.585				
4.65–123.8	94.45	56.71	0.515				
E. Carbon tetrachloride at 25°C.							
0.0 – —	9.44	7.88	0.835				
— – —	21.58	16.45	0.706				
— – —	32.95	23.86	0.652				
— – —	42.35	29.88	0.640				
— – 59.8	53.23	36.66	0.623				
59.8 – 94.96	57.67	39.03	0.534				

TABLE 3

Heats of adsorption of gases on charcoal from birchwood activated during three hours at 600°C. and outgassed at 400°C.

GREGG (31)

p mm. from — to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories	p mm. from — to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
A. C_2H_2 at 0°C.				**F. N_2O at 40.35°C.**			
0 — 3.44	6.99	2.87	0.411	0 — 46.6	7.97	3.05	0.382
3.44– 10.8	14.07	5.61	0.387	46.6 –153	17.1	6.38	0.366
10 8 – 25.8	22.14	8.36	0.340	153 –293	24.5	9.04	0.358
25 8 – 64.4	32.90	12.05	0.343	293 –718	38.5	13.93	0.349
64.4 –198.6	47.67	17.8	0.388				
198.6 –822.2	64.90	23.4	0.329	**G. SO_2 at 0°C.**			
B. C_2H_4 at 0°C.				The charcoal had been activated at 800°C. (during 4 hours) and outgassed at 400°C.			
0 — 1.18	4.27	1.54	0.360	0 — 0.43	10 8	5.69	0.528
1.18– 6.64	13.04	4.49	0.336	0 43– 1 33	27 2	13.6	0.480
6.64– 32.6	25.90	8.26	0.293	1.33– 8.61	56.9	26 6	0.440
32.6 –119	38.66	11.86	0.282	8 61– 25 0	72.7	33 3	0.421
119 –897	55.75	16.5	0.273	25 0 – 93.1	86 0	39.9	0 499
				93 1 –258	93.4	43.6	0.495
C. C_2H_6 at 0°C.				258 –838	102.2	47.0	0.392
0 — 1.91	7.49	3.20	0.427	**H. SO_2 at 40.35°C.**			
1.91– 6.10	16.45	6.78	0.399	The charcoal had been activated at 600°C. (during 3 hours), had been used for adsorption of CO, and then had been outgassed at 150°C.			
6.10– 29.3	35.26	14.13	0.391				
29.3 – 74.8	46.05	18.1	0.370				
74 8 –434.5	62.27	23.9	0.359	0 — 2.88	8.69	6.88	0.791
				2.88– 8.53	16.0	12.16	0.724
D. CO_2 at 0°C.				8.53– 21.8	32.2	20.2	0.499
0 — 6.98	4.63	1.63	0.351	21.8 – 44.7	43.5	26.4	0.547
6.98– 97.5	26.08	8.34	0.299	44.7 – 93.1	54.6	32.0	0.502
97.5 –661	57.31	17.6	0.296	93.1 –405	71.5	39.7	0.456
661 –813	60.57	18.7	0.335				
813 –964	63.13	19.9	0.363				
E. N_2O at 0°C.							
0 — 5.2	5.41	1.90	0.351				
5.2 –118	33.4	11.4	0.339				
118 –168	38.9	13.0	0.292				
168 –483	57.0	18.0	0.282				
483 –728	64.0	20.2	0.313				

TABLE 4

Heats of adsorption of carbon dioxide

A. On wood charcoal

Charcoal outgassed at 600°C.				Charcoal outgassed at 280°C.			
MAGNUS AND KALBERER				MAGNUS AND GIEBENHAIN			
p mm. from to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories	p mm. from to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
CO₂ at 0°C.				CO₂ at 0°C.			
0 – 0.0765	0.31	0.172	0.558	0 – 0.232	0.273	0.101	0.368
0.0765– 0.484	0.99	0.465	0.431	0.232– 0.413	0.467	0.171	0.362
0.484 – 0.938	1.54	0.681	0.386	0.413– 0.742	0.809	0.293	0 358
0.938 – 2.38	2.81	1.143	0.366	0.742– 1.641	1.62	0.576	0.349
2.38 – 18.3	10.4	3.680	0.336	1.641– 2.329	2.22	0.786	0 348
18.3 –150	32.7	10.57	0.308	2.329– 6.800	5.03	1.736	0.338
150 –521	50.6	15.92	0.299	CO₂ at 25°C.			
				0 – 0.517	0.184	0.063	0.340
				0.517– 0.867	0.300	0.104	0.351
				0.867– 1.905	0.626	0.216	0.344
				1.905– 4.015	1.28	0.431	0.330
				4.015– 6.300	1.92	0.645	0.332
				6.300–13.300	3 56	1.181	0.327

B. On silica gel outgassed at 350°C.

MAGNUS AND GIEBENHAIN							
CO₂ at 0°C.				CO₂ at 25°C.			
0 – 0.630	0.100	0.0330	0.330	0 – 1.350	0.0716	0.0222	0.310
0.630– 1.300	0.204	0.0673	0.330	1.350– 4.746	0.252	0.0783	0.310
1.300– 8.70	1.24	0.403	0.322	4.746– 19.15	0.942	0.285	0.300
8.70 – 36.40	4.39	1.392	0.314	19.15 – 55.90	2.58	0.783	0.304
36.40 – 92.50	9.08	2.836	0.308	55.90 –122.10	5.00	1.488	0.291

TABLE 5

Heats of adsorption of oxygen at 0°C. on wood charcoal outgassed at 1000°

MARSHALL AND BRAMSTON COOK

p mm. from — to	A ncc.	Q calories	$\dfrac{\Delta Q}{\Delta A}$ calories
0	0.0305	0.119	3.902
0	0.0907	0.324	3.400
0	0.1902	0.647	3.246
0	0.3405	1.095	2.981
0 – 0.05	0.4973	1.575	3.061
0.05– 0.40	0.7930	2.409	2.820
0.40– 6.85	1.221	3.009	1.402
6.85– 20.25	1.783	3.609	1.068
20 25– 43.50	2.493	3.840	0.325
43.50–128.2	4.823	4.472	0.271
128.2 –259.0	7.757	5.072	0.204
259.0 –374 0	10.147	5.521	0.188
374 0 –513.9	12.513	5.963	0.187

TABLE 6

Heats of adsorption of oxygen

A. On adsorbent charcoal "Norit," purified and activated at 950°C.

Temperature	A ncc. from — to		$\dfrac{\Delta Q}{\Delta A}$ calories
20°C.	0 –	0.25	3.12
57°C.	0 –	0.16	4.04
97°C.	0 –	0.18	4.82
150°C.	0 –	0.17	5.09
200°C.	0 –	0 17	5.18

B. Adsorbent: same as in A

GARNER AND MC KIE

18°C.	0.0022 0.013 ncc.	0.223
	0.09	2.68
	0.18	2.77
	0.22	3.12
	0.27	3.17
	0.34	3.17

TABLE 7
Heats of adsorption of various gases on silica gel

KÄLBERER AND SCHUSTER

p mm. from to	A ncc.	Q calories	$\dfrac{\Delta Q}{\Delta A}$ calories
A. Argon at 0°C.			
0 −103.9	0.25	0.0322	0.129
103.9–206.9	0.47	0.0670	0.158
206.9–500.5	1.09	0.178	0.179

B. N_2 at 0°C.

With N_2 on SiO_2 at 0°C. curves are found, which rise with increasing A. With various samples of SiO_2, which are different in structure, the values found diverge very much. With one sample $\dfrac{\Delta Q}{\Delta A}$ rises from 0.047 to 0.152 calories when A increases from 0 to 1.16 cc.; with another sample $\dfrac{\Delta Q}{\Delta A}$ rises from 0.064 to 0.134 calories.

C. C_2H_4 at 0°C.

With C_2H_4 at 0°C. the values of $\dfrac{\Delta Q}{\Delta A}$ differ much for various samples of the gel, but $\dfrac{\Delta Q}{\Delta A}$ always falls with increasing A, e.g.:
With sample I from 0.296 to 0.270 calories.
With sample II from 0.321 to 0.301 calories.
With sample III from 0.336 to 0.306 calories.

D. CO_2 at 0°C. and at 75°C.

With CO_2 at 0°C. curves of different types are found, according to the previous history of the gel. Whether the gel had already previously adsorbed CO_2, or even N_2, appeared to be especially important. In the case of a gel which had not yet been used for adsorption, $\dfrac{\Delta Q}{\Delta A}$ increased with increasing A from 0.280 to 0.354 calories. Also in other cases $\dfrac{\Delta Q}{\Delta A}$ varies between these values, but the shape of the curve at small concentrations is often quite different.

With CO_2 at 75°C. the following curve was found:

p mm. from to	A ncc.	Q calories	$\dfrac{\Delta Q}{\Delta A}$ calories
0 − 40.5	0.47	0.245	0.521
40.5–117.5	1.15	0.494	0.366
117.5–230	2.33	0.790	0.251
230 −359	3.59	1.106	0.251

TABLE 8

Heats of adsorption of NH_3 at $0°C$. on catalysts

DEW AND TAYLOR			
p mm. from to	A ncc.	Q calories	$\frac{\Delta Q}{\Delta A}$ calories
A. Adsorbent: Cu, from Kahlbaum's "brown label" CuO, reduced for 22 days at 140°C.			
0 -155	0.20	0.0824	0.412
155 -760	0.50	0.172	0.297
B. Adsorbent: Ni, from the nitrate, heated at 300°C. and reduced for 50 days at 300°C. The value of Q/A for H_2 on this catalyst at 0°C. is 0.668 calorie.			
0 - 62.5	0.22	0.112	0.508
62.5-212	0.34	0.165	0.423
212 -465	0.45	0.205	0.352
465 -759	0.57	0.235	0.266
C. Adsorbent: Fe, from the nitrate, heated and reduced for 30 days at 460°C.			
0 - 16	0.153	0.107	0.696
16 -102.5	0.275	0.158	0.426
102.5-368	0.376	0.203	0.437
368 -756	0.466	0.235	0.357

III. CALCULATION AND CALCULATED VALUES OF THE ISOTHERMAL HEAT OF ADSORPTION

Let there be given a volume, closed by a piston, in which one gram of adsorbent, e.g. charcoal, is in equilibrium with a gas at pressure p and temperature $T°$. Let the amount of adsorbed gas be a gram-mols, of non-adsorbed gas a' gram-mols. Let the thermodynamic potential of the charcoal with the adsorption layer be Z; then Z depends on T, p and a. Let the thermodynamic potential of the unadsorbed gas be Z'. Then $Z' = a' \, \zeta$ $(T. \, p)$, where ζ represents the thermodynamic potential of 1 gram-mol of gas and therefore depends on T and p. At equilibrium at constant p and T the thermodynamic potential is a minimum, therefore

$$\delta(Z + Z')_{p. \, T.} = 0.$$

Since

$$\delta a' = - \delta a, \quad \frac{\delta Z}{\delta a} = \frac{\delta Z'}{\delta a'}.$$

$$\frac{\delta Z'}{\delta a'} = \zeta \ (T. \ p)$$

consequently

$$\frac{\delta Z}{\delta a} = \zeta \ (T. \ p) \tag{1}$$

By pushing in the piston, a is increased by Δa, and the amount of heat ΔQ is liberated; the entropy of gas and charcoal decreases. If H' represents the entropy of the gas, and H that of the charcoal with the adsorption layer, the change of entropy is

$$- \Delta(H + H') = \frac{\Delta Q}{T}$$

The pressure is increased by $\dfrac{\delta p}{\delta a} \Delta a$ and the change of a' is

$$\Delta a' = - \Delta a.$$

Then:

$$\frac{1}{T} \frac{\Delta Q}{\Delta a} = \frac{- \Delta H - \Delta H'}{\Delta a} = - \frac{\delta H}{\delta a} - \frac{\delta H}{\delta p} \frac{\delta p}{\delta a} - \frac{\delta H'}{\delta a'} \frac{\delta a'}{\delta a} - \frac{\delta H'}{\delta p} \frac{\delta p}{\delta a} =$$

$$- \frac{\delta H}{\delta a} + \frac{\delta H'}{\delta a'} - \frac{\delta H}{\delta p} \frac{\delta p}{\delta a} - \frac{\delta H'}{\delta p} \frac{\delta p}{\delta a} \tag{2}$$

If η represents the entropy of 1 gram-mol of gas, we may write

$$H' = a' \ \eta \ (T. \ p)$$

therefore,

$$\frac{\delta H'}{\delta a'} = \eta \ (T. \ p).$$

Since $\eta = - \dfrac{\delta \zeta}{\delta T}$, we may write:

$$\frac{\delta H'}{\delta a'} = - \frac{\delta \zeta}{\delta T} \text{ and } \frac{\delta H'}{\delta p} = - a' \frac{\delta^2 \zeta}{\delta T \, \delta p}.$$

Also:

$$H = - \frac{\delta Z}{\delta T}, \text{ therefore } \frac{\delta H}{\delta a} = - \frac{\delta^2 Z}{\delta a \, \delta T} \text{ and } \frac{\delta H}{\delta p} = - \frac{\delta^2 Z}{\delta p \, \delta T}.$$

Substituting this in equation (2):

$$\frac{1}{T} \frac{\Delta Q}{\Delta a} = \frac{\delta^2 Z}{\delta a \, \delta T} - \frac{\delta \zeta}{\delta T} + \frac{\delta^2 Z}{\delta p \, \delta T} \frac{\delta p}{\delta a} + a' \frac{\delta^2 \zeta}{\delta p \, \delta T} \frac{\delta p}{\delta a} \qquad (3)$$

For two states of equilibrium with the same a but different values of p and T, the total change is:

$$\frac{\delta^2 Z}{\delta a \, \delta T} \delta T + \frac{\delta^2 Z}{\delta p \, \delta a} \delta p = \frac{\delta \zeta}{\delta T} \delta T + \frac{\delta \zeta}{\delta p} \delta p,$$

or

$$\frac{\delta^2 Z}{\delta a \, \delta T} - \frac{\delta \zeta}{\delta T} = \frac{\delta \zeta}{\delta p} \frac{\delta p}{\delta T} - \frac{\delta^2 Z}{\delta p \, \delta a} \frac{\delta p}{\delta T}.$$

Substituting this in equation (3):

$$\frac{1}{T} \frac{\Delta Q}{\Delta a} = \frac{\delta \zeta}{\delta p} \frac{\delta p}{\delta T} + a' \frac{\delta^2 \zeta}{\delta T \, \delta p} \frac{\delta p}{\delta a} + \frac{\delta^2 Z}{\delta p \, \delta T} \frac{\delta p}{\delta a} - \frac{\delta^2 Z}{\delta p \, \delta a} \frac{\delta p}{\delta T} \qquad (4)$$

In the case of an ideal gas:

$$\zeta = RT \ln p - C_p \, T \ln T + \alpha T + \beta,$$

when C_p is the specific heat at constant p, and α and β are constants. From this it follows that:

$$\frac{\delta \zeta}{\delta p} = \frac{RT}{p} \text{ and } \frac{\delta^2 \zeta}{\delta p \, \delta T} = \frac{R}{p}.$$

Substituting this in equation (4) and, for the sake of clearness, using $\left(\dfrac{\delta p}{\delta T}\right)_a$ instead of $\dfrac{\delta p}{\delta \mathrm{T}}$ etc., the equation becomes

$$\frac{\Delta Q}{\Delta a} = RT^2 \left(\frac{\delta \ln p}{\delta T}\right)_a + a' \, RT \left(\frac{\delta \ln p}{\delta a}\right)_T - T \frac{\delta}{\delta p}\left(\frac{\delta Z}{\delta a}\right)\left(\frac{\delta p}{\delta T}\right)_a + T \frac{\delta}{\delta p}\left(\frac{\delta Z}{\delta T}\right)\left(\frac{\delta p}{\delta a}\right)_T \quad (5)$$

Both of the last terms on the right hand side are negligible, since the direct influence of the pressure on a solid is very small. This holds here also, because the dependence of a on p is explicitly taken into account. We can imagine the direct influence of the pressure (at constant a) most clearly by assuming an indifferent gas, which is not at all adsorbed. Then a and p can be varied independently, and the influence of p on the condition of the solid is not measurable. The meaning of both terms can be seen clearly as follows:

$$\frac{\delta}{\delta p}\frac{\delta Z}{\delta a} = \frac{\delta}{\delta a}\frac{\delta Z}{\delta p} = \frac{\delta}{\delta a}V,$$

if V represents the volume of the charcoal with the adsorption layer. The increase of this volume at greater a is very insignificant, as well as $\dfrac{\delta}{\delta p}\dfrac{\delta Z}{\delta T} = \dfrac{\delta}{\delta T}V$, the increase of this volume per $1°$ rise in temperature at constant a.

The second term on the right hand $a'RT\left(\dfrac{\delta \ln p}{\delta a}\right)_T$ represents the heat due to compression of the unadsorbed gas. However a' is not constant, but the sum $a + a' = B$ remains constant.

$$a' \, RT \left(\frac{\delta \ln p}{\delta a}\right)_T = BRT \left(\frac{\delta \ln p}{\delta a}\right)_T - RT \left(\frac{\delta \ln p}{\delta \ln a}\right)_T.$$

The heat, due to compression from p_1 (corresponding with a_1) up to p_2 (corresponding with a_2) is

$$\int dW = BRT \int_{a_1}^{a_2} \frac{\delta \ln p}{\delta a} \, da - RT \int_{a_1}^{a_2} \frac{\delta \ln p}{\delta \ln a} \, da$$

If, according to Freundlich, the isotherms are represented by a formula $a = \alpha\, p^{\frac{1}{n}}$, in which α and $\frac{1}{n}$ are constants, then $\frac{\delta \ln p}{\delta \ln a} = n$ and is therefore constant; and the heat of compression is

$$BRT \ln \frac{p_2}{p_1} - RT\, n(a_2 - a_1)$$

In order to estimate the importance of this term, we shall calculate it with data taken from Titoff's study of NH_3 on charcoal at 0°C. When the adsorbed gas is expressed in gram-mols, we write a, when expressed in normal cubic centimeters, we write A.

Let $A_1 = 5.407$ normal cubic centimeters, $A_2 = 30.157$ normal cubic centimeters, $p_1 = 2.9$ mm., and $p_2 = 28.8$ mm. In this case $\frac{1}{n} = 0.75$, therefore $n = 1.3$. If 1 normal cubic centimeter remains unadsorbed, $B = A_2 + A' = 31.157$ normal cubic centimeters. From this we find that $\int dW = 0.95$ calorie.

The total heat effect, found by Titoff, was 12.16 calories; consequently 7.8 per cent of this should not be heat of adsorption, but should be attributed to compression. For a gas with a small heat of adsorption this error is still greater, for instance for N_2 at 0°C. (Titoff) $A_1 = 0.258$ normal cubic centimeter, $A_2 = 2.21$ cc. and 0.8 cc. remains unadsorbed. $p_1 = 10.7$ mm., $p_2 = 91.6$ mm., $\frac{1}{n}$ is 0.98, and therefore $n = 1.02$. Then $B = 3.01$ cc. From this $\int dW$ is calculated to be equal to 0.109 calorie. The total heat effect, observed by Titoff, was 0.507 calorie; therefore 21.5 per cent of this quantity should be heat of compression.

However, this derivation of the isothermal heat of adsorption does not quite correspond with the experiments. In reality the increase of pressure does not take place by moving a piston, but by admitting gas at a higher pressure. Hence in the first place $A + A'$ is not constant, and secondly we do not know exactly what really happens on the admission of gas. Possibly we get at first compression of the gas already present in the apparatus, and afterwards expansion of the remaining unadsorbed quantity; this depends on the ratio between the rate of admission of the

gas and the rate of adsorption. For this the heat effect cannot be calculated; probably the error caused by the heat of compression will be much smaller than has been calculated above. The estimation was only for the purpose of demonstrating that the heat of compression is not necessarily negligible with respect to the heat of adsorption.

Therefore

$$\frac{dQ}{dA} = RT^2 \left(\frac{\delta \ln p}{\delta T} \right)_A \tag{6}$$

the equation which also applies to the heat of evaporation. This whole derivation is of course applicable also to the heat of evaporation, if we replace the charcoal by liquid. Both terms with $\left(\dfrac{\delta p}{\delta A} \right)_T$ become 0, and $\dfrac{\delta}{\delta p} \dfrac{\delta Z}{\delta A}$ is then the change in volume of the liquid. This term also appears in the formula of Clausius-Clapeyron for the heat of evaporation; if r is the heat of evaporation

$$\frac{r}{v_1 - v_2} \qquad T \frac{dT}{dp},$$

when v_1 and v_2 represent the specific volumes of vapor and liquid; here v_2, being small compared with v_1, is also usually neglected.

Over a restricted range of temperature and pressure, equation (6) becomes

$$\frac{dQ}{dA} = \frac{R \cdot T_1 \, T_2}{T_1 - T_2} \ln \frac{p_1}{p_2}$$

Here p_1 and p_2 are the equilibrium pressures at the same A at T_1 and T_2.

The tables in and at the end of this chapter are always calculated in such a way that for a value of A, for which p_1 and T_1 are given, the corresponding p_2 is sought at T_2 by means of graphical interpolation in the isotherm. Consequently only one graphical interpolation is necessary for each calculation, and the arbitrariness attached to an interpolation, especially in a curve in which the given points are situated far from each other, becomes as small as possible.

Complete agreement between values found and those calculated cannot be expected. If gas is adsorbed without any heat, due to external work being given to the calorimeter, the value calculated ought to exceed the value found with RT. Usually this is not the case.

There are still other causes, which may explain the difference between the values found and those calculated.

1. If gas is adsorbed by a charcoal, which has been evacuated at a high temperature during a long time, the adsorption of the very first quantity is often an irreversible process. This is always the case when the gas cannot be recovered completely at the same temperature but remains bound to the adsorbent; then the derivation given above is no longer correct.

2. If the charcoal is not completely outgassed, but still contains small quantities of air, and a strongly adsorbable gas is admitted, the latter will displace the air from the charcoal. Owing to the liberation of this quantity of air, the total final pressure is higher than the partial pressure of the adsorptive; it appears therefore that a quantity smaller than the real one has been adsorbed, this quantity being determined by the difference between the admitted and the unadsorbed gas. For this reason the heat per normal cubic centimeter of gas seems higher than it really is.

However, the heat of desorption of the air driven out must be subtracted from the heat of adsorption of the gas. Therefore the error will be important only when the gas has a heat of adsorption much higher than that of air.

If we calculate the heat of adsorption from isotherms determined on charcoal which is not completely outgassed, and suppose that the same quantity of air is driven off at T_1 and T_2, and that the apparatus has the same volume, it is necessary to subtract small amounts, which are in the proportion of $T_1:T_2$, from p_1 and p_2. The ratio $p_1:p_2$ being much higher than $T_1:T_2$, the denominator of the fraction is diminished relatively more, hence the fraction becomes larger; in other words, the real heat of adsorption is greater than the heat calculated, or the calculation gives a value which is too low.

When working at pressures where the gas laws are not applicable, the experimental as well as the calculated values are found to be too low. The density of a gas is greater than has been calculated from the pressure; at definite p there is consequently less gas adsorbed than expected. Since the heat per cc. of gas is greater than we think, the experimental value is too low. The calculated value is also too low, the isotherm at high pressures being lower than the value found. The real A will therefore correspond to a greater p than that found. Because of the shape of the isotherm, the deviation from the gas laws is less important at p_2 which is smaller and lies at a lower T. Therefore the resulting values for $\dfrac{p_1}{p_2}$ and $\dfrac{dQ}{dA}$ are too low. The error depends on the so-called "dead volume" of the apparatus, but will be unimportant in most of the cases with respect to RT. Many investigators in fact take these deviations into account. From the examples it is evident that, taking everything into consideration, the agreement is satisfactory. As RT per normal cubic centimeter amounts to 0.026 calorie at 10°C., we may therefore expect this difference, and the use of the third decimal place is not justified when comparing values found with those calculated. However, the third decimal may be important in relation to the general shape of a curve.

Example I. CO_2 on charcoal (Titoff). $\dfrac{dQ}{dA}$ is calculated from isotherms at 0°C. and 30°C. $\dfrac{\Delta Q}{\Delta A}$ is measured at 0°C.

A ncc.	p at 0°C. calculated mm.	p at 30°C. mm.	$\dfrac{dQ}{dA}$ calculated calories	$\dfrac{\Delta Q}{\Delta A}$ calories	Found at A ncc.
1.82	1.2	5.3	0.363	0.345	0 to 2.3
4.02	3.6	14.7	0.344	} 0.324	2.3 " 11.3
10.3	14.2	50.7	0.311		
19.72	41.8	138.5	0.293	0.305	11.3 " 22.6
28.87	89.6	283.3	0.281	0.300	22.6 " 33.4
34.07	122.5	398.9	0.288	}	
38.14	155	498.1	0.285	} 0.294	33.4 " 43.9
41.4	189.4	621.8	0.290	}	
44.9	234	758.6	0.287	0.292	43.9 " 50.8

Example II. Methyl alcohol on charcoal. $\frac{dQ}{dA}$ is calculated from isotherms at 0°C. and 33.3°C. by Coolidge (12). $\frac{\Delta Q}{\Delta A}$ is measured at 0°C. by Lamb and Coolidge.

A ncc.	p at 0°C. calculated mm.	p at 33.3"C. mm.	$\frac{dQ}{dA}$ calculated calories	$\frac{\Delta Q}{\Delta A}$ calories	Found at A ncc.
29.7	0.057	0.9	0.615	0.619	0 to 21.7
65.4	0.33	4.1	0.563	0.553	21.7 " 47.4
				0.542	47.4 " 75.3
126.5	1.18	12.9	0.533	0.524	75.3 " 127.4

Example III. Ethyl formate on charcoal. $\frac{dQ}{dA}$ from isotherms of Coolidge (12) at 0°C. and 44.8°C. $\frac{\Delta Q}{\Delta A}$ is measured at 0°C. by Lamb and Coolidge.

A ncc.	p at 0°C calculated mm.	p at 44.8°C. mm.	$\frac{dQ}{dA}$ calculated calories	$\frac{\Delta Q}{\Delta A}$ calories	Found at A ncc.
59.2	0.060	2.08	0.607	0.598	32.3 to 62.9
76.2	0.25	6.00	0.551	0.580	62.9 " 96.7
95.5	1.10	26.7	0.549	0.568	96.7 " 120
122.8	23.5	477.6	0.519		

Even in those cases where different investigators use a different kind of charcoal the results agree fairly well. The agreement between the values for N_2 on charcoal, measured by Titoff, and those calculated from his isotherms is even worse than that between $\frac{dQ}{dA}$ and $\frac{\Delta Q}{\Delta A}$ for different charcoals, as shown in example IV.

Example IV. N_2 on charcoal. $\frac{dQ}{dA}$ is calculated from isotherms on cocoanut charcoal at 0°C. and 9.3°C. determined by Miss Homfray. $\frac{\Delta Q}{\Delta A}$ is determined by Gregg (31) at 0°C. on birchwood charcoal.

A ncc.	p at 0°C. calculated mm.	p at 9.3°C. mm.	$\frac{dQ}{dA}$ calculated calories	$\frac{\Delta Q}{\Delta A}$ calories	Found at A ncc.
1.5	68	89	0.198	0.195	0 to 3
3.5	171	216	0.171		3 " 5.5
4.6	236	316	0.214	0.209	
5.6	294	386	0.200	0.205	5.5 " 7.7
8.1	473	624	0.203	0.210	7.7 " 13.5

Example V. H_2O on charcoal. $\dfrac{dQ}{dA}$ is calculated from isotherms at 0°C. and

20°C. on sugar charcoal, determined by Coolidge (14). $\dfrac{\Delta Q}{\Delta A}$ is measured by Keyes

at 0°C. on charcoal of French gasmasks.

A ncc.	p at 0°C. calculated mm.	p at 20°C. mm.	$\dfrac{dQ}{dA}$ calculated calories	$\dfrac{\Delta Q}{\Delta A}$ calories	Found at A ncc.
0.41	0.23	0 76	0.423		
1.49	0.78	2.85	0.459		
4.21	1.48	5.5	0.465	0.381	0 to 20.6
16.3	1 85	7.2	0.481	0.474	20.6 " 60.7
191	2 77	11.6	0 507	0.472	60.7 " 102.1
198	3.20	13.2	0.502	0.467	102.1 " 143.8
208	4.00	16.8	0.508		

When comparing calculated values with those found on various types of charcoal, we must recall the curves for ether in figure 4.
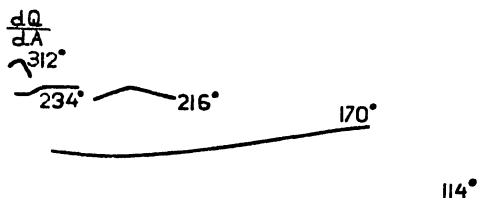
FIG. 8. ARGON ON CHARCOAL

Also from the above example of H_2O on charcoal it is evident that the general shape of the curve calculated is the same as that of the curve found. This however does not mean that at the same A the same $\dfrac{dQ}{dA}$ appears in both cases. In fact, this cannot be expected; for the quantities taken up by various charcoals at saturation with a vapor differ very much. Since the inner surfaces and inner volumes of the charcoals are different, at the same A the relative saturation is quite different. If the capacity, C, of the charcoal is the quantity taken up at the saturated pressure of the adsorptive at a certain temperature, we should compare values of $\dfrac{dQ}{dA}$ at the same $\dfrac{A}{C}$, or at the same p, but not at the

same A. Up to the present this is hardly possible, because the investigators who determine the heat of adsorption usually do not measure the pressure at all, or at most very inaccurately.

From the calculated values conclusions can now be drawn as to the influence of the temperature. In some cases this is very simple. With argon on charcoal (figure 8) or with H_2 the $\frac{dQ}{dA}$ against A curves are nearly straight, and lie higher at increasing temperatures (see tables 9A and 10D). At constant A, $\frac{dQ}{dA}$ increases much more rapidly than the absolute temperature, at
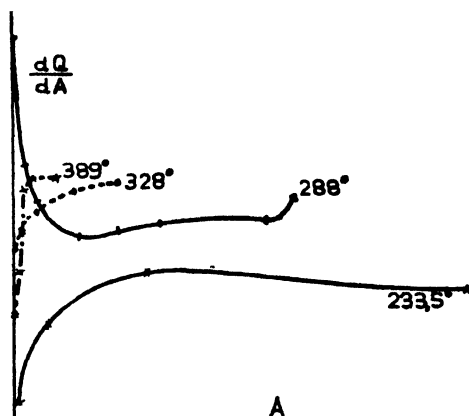
FIG. 9. N_2 ON COCOANUT CHARCOAL AT FOUR TEMPERATURES (CALCULATED FROM TITOFF'S ISOTHERMS)

least below 250° K. At $A = \pm 50$ normal cubic centimeters, $\frac{dQ}{dA}$ for argon is 0.025 calorie per normal cubic centimeter at 114°K, 0.083 calorie at 170°K and 0.161 calorie at 215°K. (The temperature mentioned is always the average of that of both isotherms, from which the values are calculated.) $\frac{dQ}{dA}$ is here approximately proportional to the third power of the absolute temperature, and to the second power at higher temperatures.

With gases which are adsorbed more strongly the relations are more complicated. Such is the case with N_2 on charcoal (fig-

ure 9). A calculation from Titoff's isotherms gives for the heat of adsorption, at 233°K as well as at 328°K and 378°K, curves, which after an initial rise, at larger values of A approach a constant value which is higher for higher temperatures (see tables 9C and 10A). The form of these curves when A is very small is unknown. It is possible that $\frac{dQ}{dA}$ lies much higher at $A = 0$ but falls steeply to a minimum and then rises again. Only then does the course discussed above set in. This at least is the shape of the curve which Polanyi and Welke calculated for SO_2 on charcoal. They determined the isotherms for very small values of A at 0°C. and at 5.3°C. on charcoal which had been evacuated during 30 days at 750°C. The curve for the heat of adsorption calculated from this has a sharp minimum at $A = 0.33$ cc. (see figure 10), and the
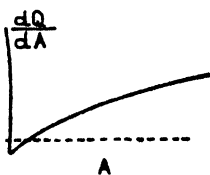
FIG. 10. SO_2 ON CHARCOAL AT 2.5°C. AND VERY SMALL CONCENTRATIONS
(Dotted line = heat of condensation of SO_2)

value of $\frac{dQ}{dA}$ in the minimum is lower than the heat of condensation of SO_2 (which is shown in the figure by a horizontal line). If the investigation had not been extended to very low concentrations, one would get the impression that this curve was of exactly the same type as that for N_2 on charcoal.

From the figure for N_2 it appears that at greater values of A the curves lie higher at a higher temperature, but that at small values this is not at all the case. That the temperature coefficient for the heat of adsorption may have a different sign when determined at different concentrations, is still more evident from the curves for ether on charcoal, calculated from the very accurate measurements of Goldmann and Polanyi (figure 11 and tables 11A and 12C). The shapes of the curves at 266°K and 283° K are

about the same (flat minimum, sharp maximum, then steep de-
cline to about the heat of condensation of ether), but at a higher
temperature the curve is shifted to the left and somewhat upward.
As the curves intersect twice, the sign of the temperature coeffi-
cient changes twice. Other vapors, such as n-pentane (see figure
14), and ethyl chloride (table 11) etc., show an analogous behavior.
For NH_3, calculated from Titoff's isotherms (table 10) only the
shifting to the left is noticeable, as at greater values of A no
pressures are measured; from the isotherms of Richardson the
difference in height is also evident (see figure 11 and table 13).
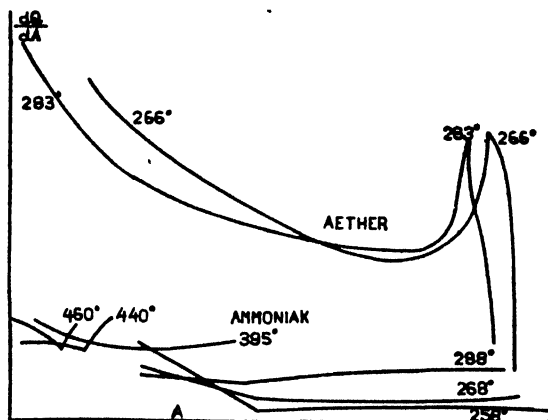
FIG. 11. ETHER ON CHARCOAL (CALCULATED FROM GOLDMANN AND POLANYI).
NH$_3$ ON CHARCOAL (CALCULATED FROM RICHARDSON)
The scale is different for the two gases.

For CO_2 it is striking that both Titoff's results (table 10) and those
of Richardson (table 13) show how much lower the heat of adsorp-
tion becomes at $\pm$ 235°K.   When A = 20 normal cubic centi-
meters (Titoff), $\dfrac{dQ}{dA}$ 0.299 calorie at 328°K, 0.293 calorie at
288°K, and 0.140 calorie at 235°K.   No influence of the critical
temperature (304°K) is noticeable.

   With the calculation from isotherms on SiO_2 etc. nothing essen-
tially new appears.   The greatest range of temperatures has been
examined here with SO_2 on SiO_2 by McGavack and Patrick (table

17).   The curves calculated for the heat of adsorption remind one of those of N_2 on charcoal.   Here also we find at 206°K as well as at 363°K a curve which rises at the beginning, while on the contrary all the curves in the neighborhood of 280°K at once fall steeply.

From the above it is evident that the curve of figure 7 for the relation between the temperature and the heat of adsorption of O_2 on charcoal at constant A is not at all an exception.   For each value of A the dependence of $\frac{dQ}{dA}$ on T will have a somewhat different course.   For many values of A there is a range where the heat of adsorption changes but little with changing T.   However, when approaching the temperature at which A is equal to the saturation quantity of the charcoal, $\frac{dQ}{dA}$ begins to rise steeply with increasing T (see figure 11).   At small values of A the temperature coefficient of $\frac{dQ}{dA}$ can be very great; in those cases no agreement can be expected between experimental and calculated values of $\frac{dQ}{dA}$, when the temperature is not exactly the same.   Yet such comparisons are often unjustly made.

If we plot $\frac{dQ}{dA}$ against p instead of against A, we find parallel lines for $\frac{dQ}{dA}$ at different temperatures in those cases where the isosteres run parallel.   For $\frac{dp}{dT}$ is constant there; at constant p the heats of adsorption must then be proportional to T^2 (or at constant $\frac{p}{RT}$ to T).   At small pressures and at pressures near saturation such a regular course is, however, out of the question.

In the following alphabetical summary of the substances, data concerning which are given in tables 9 to 19, the figures refer to the tables; the letters to the sections of the tables in which the data appear:

Charcoal as adsorbent

NH₃	A	C₂H₆	CO₂	CS₂	CO	CCl₄	CHCl₃	C₂H₅Cl	C₂H₄
10C, 13B	9A	12B	9E, 10B, 13A	11B, 12E	9F	12H	12G	11D	9D

(C₂H₅)₂O	HCOOC₂H₅	H₂	CH₄	CH₃COOCH₃	CH₃OH	N₂	C₆H₁₂	H₂O	
11A, 12C	12I	10D	9B	12F	12D	9C, 10A	11C	12A	

Other adsorbents

ADSORBENT	GAS									
	C₂H₂	C₄H₁₀	CO₂	C₂H₆	C₂H₄	H₂	CH₃Cl	NO₂	N₂O	SO₂
SiO₂..................		14	15A					16	15B	17
SnO₂..................	19A			19C	19B	19D				
Titania gel............		18A					18B			

A. Argon on cocoanut charcoal

HOMFRAY

A ncc.	p^* at	p at	$\frac{dQ}{dA}$ in calories at
	83°K	145°K	114°K
15.8	4.6	19.6	0.025
65.6	17.0	42.8	0.016
76.9	37.9	820	0.013
	145°K	194.7°K	170°K
1.4	4.0	19.0	0.078
5.1	6.0	24.0	0.070
9.7	12 4	54.2	0.074
15.4	19.0	98.4	0.083
18.6	25.6	129.0	0.081
24.0	35.0	218.0	0.092
28.8	44.2	295.0	0.096
39.4	69.2	564.0	0.106
47.0	86.4	758.0	0.109
	195°K	236°K	216°K
11.9	70.6	309.6	0.147
14.3	88.4	417.0	0.154
17.1	111.2	568.4	0.161
21.9	176.8	815.0	0.152
	194.7°K	273°K	234°K
1.6	8.0	97.5	0.150
3.8	19.0	230	0.150
5.1	24.0	319	0.156
9.7	54.2	727	0.156
	273°K	351°K	312°K
0.9	51	291.6	0.190
1.9	118	722.4	0.197
2.9	175	868.0	0.174
	351°K	373°K	362°K
1.0	77	123	0.247
2.0	155	247	0.246
3.1	254	403	0.243
5.2	454	708	0.234
	373°K	455°K	414°K
0.3	38	313	0.387
1.3	153	626	0.258

B. CH₄ on cocoanut charcoal

HOMFRAY

A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	240°K	255°K	247.5°K
11.8	36	71.4	0.247
18.5	76	153.4	0.254
24.6	132	250.2	0.231
30.8	215	412.6	0.236
33.7	270	503.2	0.225
	255°K	273°K	264°K
6.9	33.6	67	0.236
17.8	144.4	274	0.219
23.5	228.8	451	0.232
26.4	288.0	578	0.239
29.1	362.0	702	0.227
	273°K	293°K	283°K
6.9	67	132	0.240
11.4	134	260	0.235
14.1	191	362	0.226
17.8	274	527	0.232
30.7	358	685	0.230
33.5	451	854	0.228
	293°K	319°K	306°K
2.4	38	92	0.282
3.8	66	140	0.239
6.3	117	278	0.275
13.0	318	676	0.262
	319°K	351°K	335°K
2.4	92	184	0.215
3.8	140	321	0.257
6.3	278	556	0.215
7.8	347	707	0.221

* The pressure is always given in mm. of Hg.

TABLE 9—*Continued*

C. N_2 on cocoanut charcoal

HOMFRAY

A n.c.	p at	p at	$\frac{dQ}{dA}$ in calories at
	194.7°K	244.5°K	220°K
3.9	11	75	0.166
6.5	20	136	0.166
9.4	27.2	236	0.187
12.9	37.6	373	0.198
17.1	65.4	573	0.188
	244.5°K	273°K	259°K
3.9	75	197	0.200
6.5	136	351	0.197
9.4	236	590	0.190
	273°K	282.3°K	278°K
1.5	68	89	0.198
3.5	171	216	0.171
4.6	236	316	0.214
5.6	294	386	0.200
8.1	473	624	0.203

D. C_2H_4 on cocoanut charcoal

HOMFRAY

A n.c.	p at	p at	$\frac{dQ}{dA}$ in calories at
	273°K	293°K	283°K
36.7	70	177	0.329
39.8	93	228	0.318
46.4	168	426	0.330
	293°K	319°K	306°K
19.2	31	88	0.332
23.6	50	137	0.321
35.5	160	444	0.325
38.3	201	570	0.332
	319°K	351°K	335°K
19.2	88	260	0.336
23.6	137	407.5	0.338
28.0	209	639	0.346
	351°K	373°K	362°K
9.7	81	157	0.349
12.7	130	237	0.317
18.8	250	465	0.327
	373°K	405°K	389°K
11.8	210	477	0.343
14.4	297	678	0.345
17.3	403	887	0.330
	405°K	455°K	430°K
2.7	70	220	0.374
5.3	150	475	0.376
8.2	288	841	0.350

TABLE 9—*Concluded*

E. CO_2 on cocoanut charcoal				F. CO on cocoanut charcoal			
HOMFRAY				HOMFRAY			
A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at	A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	273°K	293°K	283°K		194.7°K	239 4°K	217°K
20.8	59.2	128	0.273	6.2	6	60	0.213
25.9	85.4	186	0.276	17.1	30	257.5	0.199
31.5	120	258	0.271	20.7	40	365	0.204
37.8	174	374	0.271	27.4	72	635	0.201
43.8	235	500	0.267				
					239.4°K	244.5°K	242°K
	293°K	319°K	306°K	13.8	184	229	0.222
				19.2	316	382	0.193
6.5	29	71	0.285	22.1	420	500	0.177
12.7	63	158	0.293	25.0	525	635	0.193
20.8	128	311	0.283	27.6	645	786	0.201
25.9	186	446	0.278				
31.5	258	626	0.282		244.5°K	273°K	258 8°K
				2.5	18	73	0.290
	319°K	333°K	326°K	5.5	57	180	0.239
				8.4	104	304	0.222
15.0	197	304	0.292	12.7	200	540	0.206
20.1	294	475	0.322	14.9	255	713	0.213
24.7	411	726	0.382	17.1	327	882	0.206
	319°K	351°K	335°K		273°K	293°K	283°K
6.4	70	180	0.293				
9.4	121	268	0.246	2.5	73	135	0.218
12.5	151	383	0.288	5.5	180	328	0.213
15.3	200	503	0.286	8.4	304	550	0.210
	351°K	373°K	362°K		293°K	319 2°K	306 1°K
3.2	72	127	0.299				
4.6	117	193	0.264	3.1	110	214	0.210
6.2	176	283	0.250	4.5	260	509	0.212
9.1	255	441	0.289	6.8	415	835	0.221
12.1	365	648	0.303				
14.7	479	810	0.277				
	373°K	405°K	389°K				
5.7	251	492	0.281				
8.3	391	768	0.282				
	373°K	455°K	414°K				
1.3	50	251	0.296				
2.5	98	488	0.294				
3.6	149	736	0.293				

TABLE 10

Adsorption on cocoanut charcoal

A. N_2 on cocoanut charcoal				B. CO_2 on cocoanut charcoal			
TITOFF				TITOFF			
A ncc.	p at	p at	$\dfrac{dQ}{dA}$ in calories at	A ncc.	p at	p at	$\dfrac{dQ}{dA}$ in calories at
	194°K	273°K	233.5°K		196.5°K	273°K	235°K
0.145	1.5	5.6	0.078	15.26	0.3	25.8	0.139
0.894	4.6	35.4	0.121	41.50	1.8	190.0	0.145
3.468	12.5	150	0.148	50.24	5.2	315.9	0.128
12.042	66.4	694	0.139	61.37	11.0	589.1	0.121
				65.85	14.2	755.1	0.124
	273°K	303°K	288°K		273°K	303°K	288°K
0.082	2.8	8.6	0.274				
0.227	8.8	20.3	0.204	1.82	1.2	5.3	0.363
0.766	30.4	64.5	0.184	4.02	3.6	14.7	0.344
1.718	73.2	144.6	0.166	10.29	14.2	50.7	0.311
2.764	118.6	239.6	0.172	19.72	41.8	138.5	0.293
3.875	170.0	347.6	0.175	28.87	89.6	283.3	0.281
6.646	315.6	650.0	0.176	38.14	155.0	498.1	0.285
7.490	350.4	752.3	0.187	44.93	234.0	758.6	0.287
	303°K	353°K	328°K		303°K	353°K	328°K
0.082	8.6	20.0	0.160	0.507	1.3	7.8	0.339
0.227	20.3	51.2	0.175	1.82	5.3	31.0	0.335
0.766	64.5	167.2	0.180	4.02	14.7	78.0	0.316
1.718	144.6	399.2	0.192	10.29	50.7	256	0.307
2.764	239.6	669.0	0.195	19.72	138.5	672	0.299
	353°K	424.5°K	389°K		353°K	424.5°K	389°K
0.0371	9.7	18.9	0.124	0.146	2.0	16.1	0.387
0.0754	19.0	41.8	0.146	0.378	6.0	36.6	0.336
0.1416	33.6	83.4	0.169	0.720	12.0	68.1	0.322
0.3168	69.4	194.4	0.191	1.605	28.0	154.5	0.317
0.5052	108	316.1	0.199	3.154	57.0	319.4	0.320
1.172	264	770.7	0.199	4.25	82.6	447.5	0.314
				5.78	119.2	525.2	0.275
				7.46	167.0	747.7	0.278

TABLE 10—*Concluded*

C. NH$_3$ on cocoanut charcoal				D. H$_2$ on cocoanut charcoal			
	TITOFF				TITOFF		
A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at	A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	249 5° K	273° K	261° K		194° K	273° K	233.5° K
5.5	0.3	2.6	0.563	0.0586	7.9	25.0	0.068
17.2	2.9	12.4	0.379	0.1480	19.0	66.5	0.074
45.0	16.3	49.4	0.289	0.5310	67.5	247.5	0.077
119.3	112.2	332	0.283	1.1214	141.9	530	0.078
	273° K	303° K	288° K		273° K	353° K	313° K
8.64	4.4	20.5	0.376	0.0446	19.5	73.9	0.142
19.8	15.4	62.0	0.340	0.1096	47.2	183.1	0.145
40.4	43.2	151.3	0.305	0.2538	113	454.0	0.148
60.0	75.6	269.1	0.310	0.4011	182	727.3	0.148
77.0	124	408.2	0.291				
103.5	225	785.4	0.305				
	303° K	353° K	328° K				
2.62	1.2	14.0	0.465				
3.78	4.0	27.8	0.367				
6.72	13.5	76.2	0.328				
8.64	20.5	115.0	0.327				
16.85	50.8	279.6	0.323				
24.03	80.0	431.2	0.319				
38.59	143.8	762.9	0.316				
	353° K	424.5° K	389° K				
1.02	1.6	16.6	0.434				
2.10	8.8	64.8	0.371				
3.98	30.0	176.2	0.329				
5.47	53.4	286.0	0.311				
7.20	86.0	432.7	0.300				
8.86	120.0	576.8	0.291				
10.46	151.4	721.8	0.290				

TABLE 11

Adsorption on charcoal

A. Ethyl ether on charcoal

GOLDMANN AND POLANYI

A ncc.	p at 257.7°K	p at 273°K	$\frac{dQ}{dA}$ in calories at 265.4°K
37.3	0.0175	0.0848	0.643
46.3	0.0502	0.215	0.592
68.0	0.375	1.3	0.506
89.5	1.980	6.3	0.471
107.8	7.53	24.1	0.474
113.0	12.21	42.5	0.508
117.2	23.7	100.5	0.588
119.8	43.7	174.6	0.564
122.4	78.0	184.8	0.351

A ncc.	p at 273°K	p at 293°K	$\frac{dQ}{dA}$ in calories at 283°K
23.8	0.0125	0.0844	0.676
46.0	0.212	0.980	0.542
66.8	1.295	5.01	0.479
107.2	23.0	91.6	0.490
111.0	33.5	152.8	0.538
113.0	42.6	216.2	0.575
114.7	58.5	235.5	0.493
118.1	128.2	373.4	0.378

B. CS_2 on charcoal

GOLDMANN AND POLANYI

A ncc.	p at 257.7°K	p at 273°K	$\frac{dQ}{dA}$ in calories at 265.4°K
42.4	0.065	0.228	0.511
63.8	0.245	0.761	0.462
95.2	0.849	2.46	0.504
117.2	1.64	4.56	0.416
150.3	3.77	10.5	0.417
183.9	9.7	28.0	0.427
195.7	18.9	54.0	0.427

A ncc.	p at 273°K	p at 293°K	$\frac{dQ}{dA}$ in calories at 283°K
21.7	0.0294	0.154	0.573
42.2	0.226	0.931	0.490
63.2	0.74	2.78	0.458
93.4	2.3	8.20	0.440
114.0	4.3	14.5	0.421
143.8	9.1	29.0	0.401
171.6	17.2	57.0	0.415
189.5	35.0	114.8	0.411
202.0	94.0	271.3	0.367

TABLE 11—*Concluded*

C. *n*-Pentane on charcoal				D. Ethyl chloride on charcoal			
GOLDMANN AND POLANYI				GOLDMANN AND POLANYI			
A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at	A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	209.3°K	257.7°K	233 5°K		257.7°K	273°K	265.4°K
100.2	0.024	3.6	0.494	16.1	0.0177	0.065	0.530
112.1	0.067	8.6	0.478	22.9	0.0479	0.175	0.528
122.6	0.233	50.0	0.529	40.5	0.289	0.896	0.461
124.3	0.288	72.3	0.544	66.6	1.410	3.99	0.424
				119.9	12.02	30.5	0.379
	257.7°K	273°K	265 4°K	131.1	17.81	47.0	0.395
				150.1	35.6	91.3	0.384
46.8	0.034	0.1405	0.582	161.5	58.4	168	0.430
67.6	0.25	0.89	0.521	168.1	105.7	304	0.430
81.7	0.83	2.5	0.452	170.1	131.1	316	0.342
90.2	1.6	5.0	0.467				
105.0	5.0	14.6	0.439		273°K	293°K	283°K
112.8	9.1	29.2	0.478				
116.0	13.2	45.4	0.507	9.26	0.014	0.0678	0.559
118.8	20.0	80.7	0.572	20.8	0.135	0.552	0.499
121.7	39.3	161.0	0.578	49.2	1.61	5.60	0.442
				91.1	11.2	35.8	0.412
	273°K	273 2°K	275.6°K	114.6	26.7	82.7	0.400
				127.0	41.2	124.8	0.423
81.7	2.5	3.9	0.571	141.9	68.2	204.2	0.388
90.2	5.0	7.4	0.503	152.9	101.7	311.1	0.396
105.0	14.6	21	0.467	158.8	138.0	448.0	0.417
116.0	45.4	68	0.519				
118.8	80.7	126	0.572				
	273°K	293.5°K	283 2°K				
37.6	0.0533	0.284	0.579				
50.6	0.203	0.99	0.548				
67.6	0.89	3.86	0.508				
90.2	5.0	21.2	0.500				
105.0	14.6	55.6	0.463				
112.8	29.2	138	0.538				
116.0	45.4	254	0.596				
118.8	80.7	390	0.545				

TABLE 12

Adsorption on charcoal

A. H_2O on sugar charcoal

COOLIDGE

The following isosteres are taken from Coolidge (14) p. 715, table III.

A ncc.	p 243°K	p 273°K	p 293°K	p 334°K	p 373°K	p 429°K
0.41	0.0175	0.23	0.76	5.8	20.5	76
1.49	0.066	0.78	2.85	19.5	74	257
4.21	0.125	1.48	5.5	45	173	710
16.3	0.16	1.85	7.2	68	330	1500
191	0.22	2.77	11.6	120	760	
198	—	3.20	13.2	142		
208	0.28	4.00	16.8			

From this is calculated:

A ncc.	$\frac{dQ}{dA}$ at 258°K calories	283°K	313.5°K	353.5°K	401°K
0.41	0.505	0.423	0.428	0.357	0.332
1.49	0.484	0.459	0.409	0.377	0.315
4.21	0.484	0.465	0.443	0.381	0.357
16.3	0.479	0.481	0.475	0.447	0.383
191	0.496	0.507	0.494	0.522	
198	—	0.502	0.502		
208	0.521	0.508			

The measurements of organic vapors on cocoanut charcoal by Coolidge cover a wide range of temperatures, but are less accurate than those of Goldmann and Polanyi (table 11).

Heats of adsorption are calculated partly from isosteres which Coolidge interpolated from his isotherms and published (J. Am. Chem. Soc. **46**, 596 (1924)), partly from the original isotherms which Coolidge kindly sent us and for which we wish to express our gratitude.

The unpublished values are used in those cases, where a more accurate value for the heat of adsorption could be expected by taking temperatures closer to each other and diminishing the number of interpolations.

Values taken from Coolidge's isosteres are marked *.

The third decimal of the values of $\dfrac{dQ}{dA}$ and the pressures may be omitted.

TABLE 12—*Continued*

B. Benzene on cocoanut charcoal

*Between 273°K and 333°K		*Between 333°K and 423°K	
A ncc.	$\dfrac{dQ}{dA}$ at 303°K calories	A ncc.	$\dfrac{dQ}{dA}$ at 378°K calories
25	0.65	5	0.74
50	0.61	25	0.64
75	0.58	50	0.59
100	0.56	75	0.56

Between 420.5°K and 489°K		Between 489°K and 576°K	
A ncc.	$\dfrac{dQ}{dA}$ at 454°K calories	A ncc.	$\dfrac{dQ}{dA}$ at 532.5°K calories
6.3	0.73	0.8	0.85
10.8	0.72	1.9	0.79
		2.6	0.76
		7.1	0.69

TABLE 12—*Continued*

C. Ethyl ether on cocoanut charcoal

COOLIDGE

Between 273°K and 306°K		Between 306°K and 332°K	
A ncc.	$\frac{dQ}{dA}$ at 289.5°K calories	A ncc.	$\frac{dQ}{dA}$ at 319°K calories
57	0.60	32	0.64
78	0.56	58	0.49
86	0.60	90	0.54
91	0.53		
106	0.47		

Between 332°K and 372°K		Between 372°K and 420°K	
A ncc.	$\frac{dQ}{dA}$ at 352°K calories	A ncc.	$\frac{dQ}{dA}$ at 396°K calories
21	0.63	14	0.69
32	0.57	21	0.64
58	0.51	32	0.59
		57	0.53

Between 420°K and 489°K		Between 489°K and 576°K	
A ncc.	$\frac{dQ}{dA}$ at 454.5°K calories	A ncc.	$\frac{dQ}{dA}$ at 532.5°K calories
		1.1	1.14
8	0.79	2.2	1.03
14	0.63	3.1	0.96
21	0.60	5.9	0.76
31	0.57	7.7	0.69
		14	0.79
		20	0.67
		22.4	0.59

D. Methyl alcohol on cocoanut charcoal

COOLIDGE

Between 273°K and 306.3°K		*Between 323°K and 373°K	
A ncc.	$\frac{dQ}{dA}$ at 289.6°K calories	A ncc.	$\frac{dQ}{dA}$ at 348°K calories
30	0.62	10	0.71
65	0.56	20	0.58
126	0.53	30	0.55
173	0.50	100	0.50
194	0.47	150	0.49
220	0.52		
237	0.52		
241	0.50		
251	0.46		

*Between 373°K and 423°K	
A ncc.	$\frac{dQ}{dA}$ at 398°K calories
5	0.88
10	0.71
20	0.56
30	0.52
100	0.48

TABLE 12—*Continued*

E. Carbondisulfide on cocoanut charcoal				G. Chloroform on cocoanut charcoal			
COOLIDGE				COOLIDGE			
*Between 273°K and 333°K		*Between 333°K and 423°K		Between 273°K and 317.8°K		Between 317.8°K and 372°K	
A ncc.	$\frac{dQ}{dA}$ at 303°K calories	A ncc.	$\frac{dQ}{dA}$ at 378°K calories	A ncc.	$\frac{dQ}{dA}$ at 295.4°K calories	A ncc.	$\frac{dQ}{dA}$ at 344.9°K calories
				71	0.55	47	0.55
25	0.53	5	0.56	94	0.55	67	0.54
75	0.48	25	0.51	103	0.45	70	0.55
150	0.46	75	0.47	118	0.56	95	0.55
		100	0.45	123	0.46		

Between ± 422°K and 489°K		Between 489°K and 576.8°K		H. Carbon tetrachloride on cocoanut charcoal			
				COOLIDGE			
A ncc.	$\frac{dQ}{dA}$ at 455 5°K calories	A ncc.	$\frac{dQ}{dA}$ at 533°K calories	Between 273°K and 317.6°K		Between 317.6°K and 371.6°K	
2.1	0.61			A ncc.	$\frac{dQ}{dA}$ at 295.3°K calories	A ncc.	$\frac{dQ}{dA}$ at 344 6°K calories
3.2	0.58	3.1	0.58				
4.1	0.55	8.1	0.44	75	0.58	44	0.52
10	0.48	20	0.55	88	0.58	66	0.57
15	0.42					73	0.59
						81	0.56

F. Methyl acetate on cocoanut charcoal	
COOLIDGE	
*Between 273°K and 373°K	
A ncc.	$\frac{dQ}{dA}$ at 323°K calories
50	0.58
75	0.56
100	0.55

TABLE 12—*Concluded*

I. Ethyl formate on cocoanut charcoal

COOLIDGE

Between 273°K and 317.7°K		Between 317.7°K and 371.8°K	
A ncc.	$\frac{dQ}{dA}$ at 295.3°K calories	A ncc.	$\frac{dQ}{dA}$ at 344.7°K calories
59	0.61	26	0.61
76	0.55	43	0.58
95	0.55	59	0.52
123	0.52	76	0.55
		96	0.53

The determinations of Richardson cover a very large stretch of p and T. However they are not very accurate, since Richardson outgassed his charcoal at too low a temperature (400°C.); therefore he found differences of many per cents in pressure, whether working at rising or decreasing T. Hence the third decimal of $\frac{dQ}{dA}$ and the pressures may be omitted.

TABLE 13
Adsorption on cocoanut charcoal

A. CO_2 on cocoanut charcoal

RICHARDSON

Between 209°K and 219°K

A ncc.	$\frac{dQ}{dA}$ at 214°K calories
44	0.17
64	0.11
87	0.08
99	0.17
104	0.17

Between 230°K and 243°K

A ncc.	$\frac{dQ}{dA}$ at 236.5°K calories
22	0.26
43	0.23
63	0.18
82	0.26
88	0.29

Between 243°K and 253°K

A ncc.	$\frac{dQ}{dA}$ at 248°K calories
12	0.25
22	0.33
43	0.28
61	0.28
80	0.27

Between 263°K and 273°K

A ncc.	$\frac{dQ}{dA}$ at 268°K calories
11	0.22
21	0.27
41	0.28
56	0.33
71	0.25

Between 273°K and 283°K

A ncc.	$\frac{dQ}{dA}$ at 278°K calories
11	0.28
21	0.32
40	0.29
62	0.26
68	0.25
71	0.29

Between 388°K and 403°K

A ncc.	$\frac{dQ}{dA}$ at 395.5°K calories
6	0 34
10	0.36
16	0.58

Between 403°K and 418°K

A ncc.	$\frac{dQ}{dA}$ at 410.5°K calories
4	0.34
7	0.32
10.6	0.36
11.1	0.59
12.5	0.67

B. NH_3 on cocoanut charcoal

RICHARDSON

Between 253°K and 263°K

A ncc.	$\frac{dQ}{dA}$ at 258°K calories
26	0.36
46	0.15
69	0.15
91	0.13
113	0.13
134	0.21

Between 263°K and 273°K

A ncc.	$\frac{dQ}{dA}$ at 268°K calories
26	0.28
46	0.18
68	0.18
90	0.19
111	0.21
128	0.28
141	0.28

Between 283°K and 293°K

A ncc.	$\frac{dQ}{dA}$ at 288°K calories
26	0.27
45	0.22
66	0.27
87	0.28
105	0.33
128	0.29

Between 313°K and 328°K

A ncc.	$\frac{dQ}{dA}$ at 320.5°K calories
13	0.35
25	0.35
43	0.30
63	0.33
96	0.34

Between 328°K and 343°K

A ncc.	$\frac{dQ}{dA}$ at 335.5°K calories
12	0.34
23	0.37
53	0.36
76	0.35
91	0.34

Between 373°K and 388°K

A ncc.	$\frac{dQ}{dA}$ at 380.5°K calories
11	0.35
20	0.32
32	0.31
42	0.29
50	0.30

TABLE 13—*Concluded*

B. NH₃ on cocoanut charcoal— *concluded*

Between 388°K and 403°K		Between 433°K and 448°K	
A noc.	$\frac{dQ}{dA}$ at 395.5°K calories	A noc.	$\frac{dQ}{dA}$ at 440.5°K calories
9	0.43	7	0.37
16	0.37	12	0.37
25	0.34	18	0.34
31	0.32	22	0.45
36	0.33		
43	0.36		

Between 448°K and 473°K	
A nec.	$\frac{dQ}{dA}$ at 460.5°K calories
5	0.44
8	0.42
11	0.39
14	0.35
15	0.40

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TABLE 14

Adsorption on silica gel

Butane on silica gel (containing ±3.5 per cent H_2O)

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A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	273°K	303°K	288°K
3.8	7.41	28	0.325
10.6	32.89	110	0.295
20.7	86.85	272	0.279
35.2	167.13	512	0.273
	303°K	313°K	308°K
3.1	19.45	34.5	0.481
6.3	51.03	81.0	0.388
8.0	77.20	114.5	0.331
14.6	169.4	250.0	0.327
15.4	187.2	268.5	0.303
21.8	287.3	410	0.299
32.1	456.2	637	0.280
	313°K	373°K	343°K
1.9	18	145.39	0.360
3.4	40	294.66	0.344
6.2	80.5	566.89	0.336
7.5	103.5	696.46	0.329

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PATRICK AND LONG

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<div align="center">TABLE 15</div>

<div align="center">*Adsorption on silica gel*</div>

A. CO_2 on silica gel containing ± 1.3 per cent H_2O				B. N_2O on silica gel containing ± 1.4 per cent H_2O			
PATRICK, PRESTON AND OWENS				PATRICK, PRESTON AND OWENS			
A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at	A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	273°K	293°K	283°K		273°K	293°K	283°K
1.45	68.82*	163 5	0.31	1.9	107	189.31	0.20
2.8	149.88	319	0.27	3.1	182.5	344.05	0.22
3.4	182.11	390	0.27	3.7	225	453.46	0.25
4.6	259.78	545	0 26	4 0	238	496.46	0.26
	293°K	303°K	298°K		293°K	303°K	298°K
0 62	61.28	77.5	0.18	0 77	68.90	111.6	0.38
1.57	162.81	229	0.27	1.9	189.31	277.8	0.30
2.7	297 32	420	0.27	3 1	344.05	463.2	0.23
3.9	456.64	622.5	0.24		303°K	313°K	308°K
	303°K	313°K	308°K	0.71	109.8	207.19	0.53
0.62	77.5	97.29	0.19	0.99	148.8	308.55	0.61
1.4	201.5	257.12	0.20	1.6	235.8	457.07	0.56
2.1	326	408.82	0.19	2.0	286.8	550.68	0.55
2.7	423.5	549.99	0.22				
3.2	505	625.44	0.18				

* Since control determinations diverge very much, only two decimals are given.

TABLE 16

Adsorption on silica gel

N_2O_4 on silica gel containing ±6 per cent H_2O

RAMES RAY

The amount adsorbed, A', is given in milligrams per gram of gel. Since the molecular weight of N_2O_4 varies with T, the calculation in ncc. is impossible.

A'	p at	p at	$\frac{dQ}{dA'}$ in calories at
milligrams	288° K	330° K	309° K
41.4	1.0	11	0.481
64.2	2.5	30	0.498
95.9	5.0	88	0.575
121.7	7.5	150	0.600
157.8	13.7	270	0.597
178.0	18.8	351	0.587
196.5	25.0	450	0.579
204.6	28.6	490	0.569
	330° K	353° K	341.5° K
41.4	11	44.0	0.783
64.2	30	101.6	0.689
95.9	88	234.4	0.553
121.7	150	338.0	0.459
	353° K	373° K	363° K
18.4	10.0	30	0.641
35.6	32.6	88	0.579
48.9	60.0	150	0.534
68.5	115.0	270	0.498
80.7	151.0	351	0.492
93.8	205.8	450	0.456
99.2	230.0	490	0.441

TABLE 17

Adsorption on silica gel

SO$_2$ on silica gel

MC GAVACK AND PATRICK

A ncc.	p at	p at	$\frac{dQ}{dA}$ in calories at
	193°K	219°K	206°K
50.3	0.13	1.3	0.332
98.8	0.58	7.4	0.363
148	1.65	19	0.352
182	3.05	32.2	0.339
207	4.60	44.0	0.325
230	8.30	56.0	0.275
	238.6°K	273°K	255.8°K
53.3	4.22	42.2	0.387
81.5	13.85	112	0.351
108.2	29.02	219.6	0.340
137.2	50.07	364.6	0.334
162.6	73.45	514.0	0.327
192.7	116.62	720	0.306
	273°K	303°K	288°K
11.8	0.8	9.50	0.614
25.7	8.4	40.56	0.390
36.5	18.4	82.32	0.372
47.8	32.0	141.46	0.369
61.3	58.6	241.77	0.351
77.5	100	408.02	0.349
99.3	182	702.40	0.335
	330°K	353°K	341.5°K
4.5	12	47.0	0.612
16.7	70.4	192.19	0.451
18.7	83.2	224.73	0.446
27.7	191.4	407.88	0.339
34.2	286	575.32	0.313
37.4	344	671.95	0.300
	353°K	373°K	363°K
6.6	71.6	105.88	0.228
12.0	134.6	229.93	0.312
17.8	208	397.00	0.377
22.0	268.2	544.20	0.413
24.6	342	671.50	0.393

TABLE 18
Adsorption on titania gel

A. Butane on titania gel

Between 273°K and 308°K

A ncc.	$\frac{dQ}{dA}$ at 290.5°K in calories
12.7	0.33
15.2	0.33

B. Methyl chloride on titania gel

Between 298°K and 318°K

A ncc	$\frac{dQ}{dA}$ at 308°K in calories
17.6	0.29
21.0	0.29
21.9	0.31

TABLE 19
Adsorption on SnO_2

A. C_2H_2 on SnO_2*

Between 273°K and 351.5°K

A ncc	$\frac{dQ}{dA}$ at 312°K in calories
0.073	0.17
0.108	0.16
0.141	0.17
0.174	0.15
0.254	0.15

B. C_2H_4 on SnO_2

Between 273°K and 351.5°K

A ncc.	$\frac{dQ}{dA}$ at 312°K in calories
0.071	0.19
0.131	0.19

TABLE 19—*Concluded*

Between 351.5°K and 373°K	
A ncc.	$\frac{dQ}{dA}$ at 362°K in calories
0.020	0.19
0.038	0.20
0.057	0.16
0.084	0.20
0.112	0.25

C. C_2H_6 on SnO_2

PEARCE AND GOERGEN

Between 273°K and 351.5°K	
A ncc.	$\frac{dQ}{dA}$ at 312°K in calories
0.86	0.18
1.49	0.18

Between 351.5°K and 373°K	
A ncc.	$\frac{dQ}{dA}$ at 362°K in calories
0.019	0.43
0.036	0.45
0.054	0.39
0.070	0.38
0.090	0.32
0.107	0.30
0.136	0.27

D. H_2 on SnO_2

PEARCE AND GOERGEN

Between 273°K and 351.5°K	
A ncc.	$\frac{dQ}{dA}$ at 312°K in calories
0.006	0.075
0.009	0.075
0.018	0.099

* The heat of adsorption varies very much with the previous history and the water content of the SnO_2.

IV. STATE OF THE ADSORBED PHASE

From the standpoint of phase-equilibria the adsorption-layer is not a separate phase, but forms with the adsorbent one phase of variable composition. The system has two components, and two degrees of freedom and consequently can have only two phases. If however we mean by a "phase" a complex of identical units of volume (in which the unit must be thought very small), the adsorption-layer is not merely a separate phase, but may contain two and even more phases. The conditions for the equilibrium between three- and two-dimensional phases, such as they appear in monomolecular adsorption-layers, have been traced by Ehrenfest. He found that the pressures in the two-dimensional phases must be mutually equal, but that thermodynamically no relation can be found between the two- and the three-dimensional pressures. When adsorption of a vapor on charcoal takes place, the adsorption-layer will be in gaseous condition, in case a very small quantity has been adsorbed, i.e. the molecules are free to move within the surface. At a somewhat greater concentration we get coexistence between liquid and gas in the interface. From this the question arose as to the pressure in the adsorption-layer; the estimates vary between 30,000 atmospheres and a negative pressure. The following arguments are advanced in favor of a high pressure:

1. Lamb and Coolidge calculated the net heat of adsorption (= heat of adsorption minus heat of condensation) per unit of volume of liquid adsorbed and found that for various substances this quantity is almost the same. If, in accordance with their opinion, the net heat of adsorption arises exclusively from compression, the pressure in the adsorption layer can be found by dividing the net heat of adsorption by the heat of compression per atmosphere of the liquid. In this way 28,000 to 37,000 atmospheres was found for the pressure in various liquid layers.

2. The volumes of liquid adsorbed by the charcoal at saturation do not differ much, and the greatest volume nearly always belongs to the liquid with the greatest compressibility.

3. According to determinations made by Harkins and Ewing, Williams (89), Cude and Hulett, the specific volume of charcoal

seems to vary with the liquid used in the pycnometer. The greater the compressibility of the liquid, the smaller the specific volume found for the charcoal. The explanation lies at hand: the more compressible the liquid, the greater the difference between its real volume at high pressure and that calculated; the smaller, therefore, is the specific volume of the charcoal.

4. The net heat of adsorption of water on charcoal at 0°C. is negative, according to Keyes' determinations. As the temperature increases from 0°C. the density of water becomes greater and the heat of compression is therefore negative. Here also the net heat of adsorption can be explained by compression at a high pressure.

TABLE 20

Heats of wetting of charcoal

LIQUID	HEAT OF WETTING		
	Of bone black calories	Of sugar charcoal dried at 100°C. calories	Of sugar charcoal dried at 1200°C. calories
Water..	18.5	3.9	—
Acetone......................................	19.3	3.6	28.6
Methyl alcohol	17.6	11.5	—
Ethyl alcohol...............	16.5	6.9	23.3
Ethyl ether................................	—	1.2	—
Chloroform................................	14.0	2.3	—
Carbon tetrachloride......................	8.4	1.5	—
Carbon disulfide..........................	13.9 ·	4.0	31.2
Benzene....................................	11.1	4.2	32.7

According to this representation, the emphasis lies upon the inner volume of the charcoal, not upon the surface. One might suppose that the quantity adsorbed at saturation could exactly fill a monomolecular layer. Then the surface, covered by this quantity, should always be equal for various liquids. However, the percentage differences between the surfaces calculated in this way are much greater than those between the volumes, so that the supposition of a monomolecular layer offers no advantage here.

There are, however, many objections to the arguments of Lamb and Coolidge:

1. The net heat of adsorption, which is equal to the heat of wetting, cannot be always the same for one sort of charcoal, independent of the nature of the liquid. Since the charcoal takes up almost equal quantities at saturation, the heats of wetting per gram of charcoal should also be nearly equal. However the heats of wetting indicate that this is not true at all, even for those organic liquids tested by Lamb and Coolidge.

Gurvic made determinations with bone black, Gaudechon with sugar charcoal dried at 100°C., and Bartell and Ying Fu with sugar charcoal, dried at 1200°C.; their results for the heat of wetting per gram of charcoal are shown in table 20.

From this it is evident that the percentage differences are very great, especially for Gaudechon's sugar charcoal. For bone black (which has a larger ash content) they approach, save for a single exception, the order of magnitude found by Lamb and Coolidge for the differences between the net heats of adsorption, (i.e. about 25 per cent).

2. Heat of adsorption cannot be caused merely by compression, as shown by Coolidge (13) in a more recent article, since it is greatest for the first quantities of gas, which do not find anything to compress. The loss of potential energy at the near approach of the charcoal is not equivalent to a heat of compression from all sides. An adsorbed layer can be compressed only by the layers lying above it, which are also attracted by the charcoal. Here we have to do not only with the attraction between adsorbent and adsorptive, but also with the mutual attraction between molecules of the adsorptive. This influence will be especially evident in the case of a vapor condensing on the charcoal.

We shall try to develop this idea quantitatively, in order to come to an estimate (a rather approximate one, perhaps) of that part of the heat of adsorption which we can explain by compression.[3]

We therefore suppose a constant volume, to which we gradually admit more vapor, for instance by communication with a volume in which the pressure is somewhat higher. The differences in

[3] Of course this heat of compression has nothing to do with the heat which we calculated for the compression of the unadsorbed gas.

pressure must always be very small, so that we can disregard the heat of expansion of the gas admitted. Heat of compression is then continually developed, and the total quantity of heat, U (from the initial condition with no volume up to a quantity A), is exclusively a function of A.

For the heat of compression of 1 gram-mol, we may write the formula of Maxwell:

$$\left(\frac{dQ}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v,$$

if v represents the molecular volume and Q the heat absorbed. The heat of compression of A gram-mols,

$$dU = -A\,dQ = -AT\left(\frac{dp}{dT}\right)_v dv.$$

If V is the constant total volume, $v = \dfrac{V}{A}$, consequently

$$dv = -\frac{V}{A^2}\,dA$$

and

$$\frac{dU}{dA} = T\frac{V}{A}\left(\frac{dp}{dT}\right)_v = T\left(\frac{dp}{dT}\right)_v v.$$

As long as the gas laws are applicable,

$$\frac{dp}{dT} = \frac{R}{v},$$

consequently

$$\frac{dU}{dA} = RT.$$

As soon as the vapor is saturated, p does not change any more, and as $v = \dfrac{RT}{p}$, we find

$$\frac{dU}{dA} = RT^2\frac{\delta \ln p}{\delta T},$$

and consequently the heat of condensation. As v is always the molecular volume of the vapor admitted, $\dfrac{dU}{dA}$ remains constant

until everything is condensed and the volume is filled with liquid.

Then $\left(\dfrac{dp}{dT}\right)v$ immediately rises rapidly, the compressibility of a liquid being very small. In order to follow the adsorption process as closely as possible, let us suppose that saturated vapor, which immediately condenses, is admitted; then $\dfrac{dU}{dA}$ equals the heat of condensation of the vapor admitted plus $T\left(\dfrac{dp}{dT}\right)v$, in
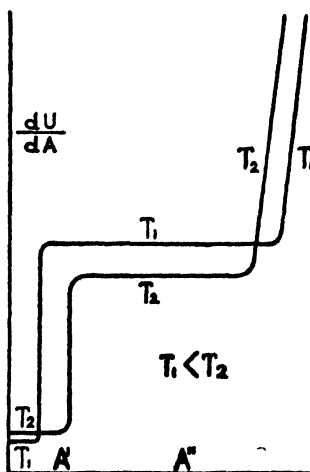
FIG. 12. CHANGE OF $\dfrac{dU}{dA}$ WITH A AT TWO TEMPERATURES

which v is now the molecular volume of the liquid. If we now calculate the curve for ether at 0°C., $\dfrac{dU}{dA}$ per normal cubic centimeter is at first 0.024 calorie, at condensation it is 0.297 calorie and afterwards, when the liquid is being compressed, it is 0.297 + 0.506 = 0.803 calorie per normal cubic centimeter.

The value of A, at which condensation appears, is $A' = \dfrac{p'V}{RT}$, in which p' is the saturated vapor pressure. For higher values of T, A' is larger, since p' increases more than T. The heat of condensation falls with increase of temperature; RT however

has increased. The point A'', where the volume is entirely filled with liquid, is situated at higher T at lower A, owing to the dilatation of the liquid. The curves for two temperatures will therefore intersect twice, and will have the course as shown in figure 12.

If we now place the constant volume of our derivation on a par with the volume taken up by the first layer, we see that the heat of compression will increase strongly as soon as the first layer is filled. The value of 0.8 calorie per normal cubic centimeter of ether will not be reached however, for when the liquid is compressed in the first layer, the point is reached at which a newly admitted quantity of vapor forms a second layer more easily than it attains a place in the first layer. This second layer is subjected to forces from the adsorbent as well as from the first layer and therefore compresses the latter. The heat of compression thus liberated cannot be calculated quantitatively; that it may be important is shown from the following reasoning.

The second layer does not evaporate (for the sake of convenience we consider the equilibrium as being static) in spite of the fact that the pressure is smaller than the saturated vapor-pressure. If, however, the same liquid were present in place of the charcoal, the second layer would evaporate immediately. The force exercised by the charcoal on this second layer must therefore be so much greater than that of the liquid itself at the same distance, that it neutralizes the lowering of the vapor-pressure. If, for instance, the pressure is one-tenth of the saturated tension, the attraction of the charcoal is ten times greater than that of the liquid at the same place. The first layer, therefore, is situated between two layers which attract each other ten times more strongly than in the normal liquid; therefore the compression will be about ten times the normal inner pressure. If we estimate the inner pressure for ether at 0°C. according to van der Waals to be 1400 atmospheres, the compression of the first layer is 14,000 atmospheres. The heat liberated when one cubic centimeter of liquid is compressed, is for ether at 0°C. equal to 0.00298 calorie per atmosphere (average between 1 and 12,000 atmospheres). (This value was calculated by Lamb and Coolidge

from Bridgeman's measurements.)   For 14,000 atmospheres this becomes 41.7 calories.   If, for instance, 0.2 cc. of liquid is present in the first layer, 8.3 calories of heat of compression are liberated when the second layer has been formed.   If also 0.2 cc. of liquid = 44.4 normal cubic centimeters of vapor have come in the second layer, about 0.19 calorie per normal cubic centimeter has been contributed to the heat of adsorption by the heat of compression of the first layer.

This estimate is only approximate, for: (1) the influence exerted by the charcoal on the second layer is partly indirect, owing to the changes brought about in the first layer; (2) if only the first layer is present, it is not under normal inner pressure; (3) the heat of compression will not be constant for each normal cubic centimeter which comes into the second layer.

We do not know at all how the formation of the second layer is effected, and cannot trace therefore, how the heat of compression will be distributed over the next quantity adsorbed.   If, as soon as the second layer is filled, a third layer is formed, the attraction of the charcoal will have decreased much more than the compressible quantity of liquid has increased.   The heat of compression will therefore be much smaller than at the formation of the second layer, and will always become smaller for possible following layers.

We shall now compare the curve calculated for $\frac{dU}{dA}$ with the curve for $\frac{dQ}{dA}$, found by Lamb and Coolidge at 0°C. for ether on cocoanut charcoal (figure 13).   The straight part in the $\frac{dQ}{dA}$ curve must agree with the rise of the $\frac{dU}{dA}$ curve, and therefore shows us where the second layer is filled.   This begins at about $A = 23$ normal cubic centimeters; this quantity of ether covers as monomolecular liquid layer a surface of 188 square meters, if we take for the thickness of the layer the cube root of the volume of one molecule.

As the ether molecules are probably orientated, it is more exact

to take for the section of the molecule parallel to the surface of the charcoal, the value of about $0.20m\mu^2$, found by Adam for many organic substances with straight chains. The surface of one gram of the charcoal of Lamb and Coolidge amounts then to 139 square meters. In the same way we calculate from the ether curve of Keyes for his charcoal a specific surface of 100 square meters.
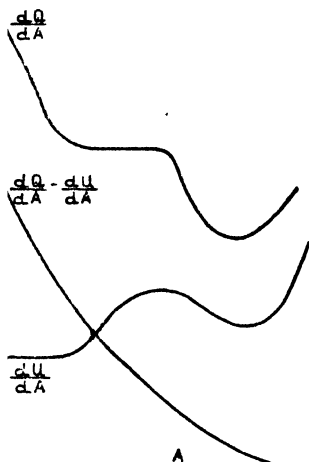
FIG. 13. ETHER ON CHARCOAL AT 0°C.

Heat of adsorption (measured by Lamb and Coolidge), heat of compression and real heat of adsorption. The value of $\dfrac{dQ}{dA}$ of the abscissa is 0.15 calorie.

If we now draw $\dfrac{dQ}{dA} - \dfrac{dU}{dA}$ against A, we get a curve which goes down regularly, and represents the heat of adsorption which we should find if we could avoid the heat of compression. We call this the "real heat of adsorption" (the expression "net heat of adsorption" would be preferable, if Lamb and Coolidge and many others had not used "net heat of adsorption" for the "heat of wetting"). The meaning of this "real heat of adsorption" will be discussed later on.

With ether the fall of the "real heat of adsorption" is compensated by the rise of $\dfrac{dU}{dA}$, whereby $\dfrac{dQ}{dA}$ remains constant therefore

over a rather long distance. This is an exception. If the heat of compression is smaller in proportion to the real heat of adsorption, $\frac{dQ}{dA}$ will continue to go down slowly; if the heat of compression is greater in proportion to the "real heat of adsorption" than in the case of ether, $\frac{dQ}{dA}$ will rise slowly. Especially if $\frac{dU}{dA}$ is small, it is very difficult to deduce from the curve for the heat of adsorption where the second layer is formed.

Lamb and Coolidge have not continued their determinations up to the point of saturation. However, it is possible to deduce the further course of these curves from the isotherms measured by Goldmann and Polanyi (see figure 11). Just before saturation, $\frac{dQ}{dA}$ rises steeply and then falls to the heat of condensation. This rise cannot be attributed to heat of compression, but probably is due to the heat liberated when a large liquid-air interface disappears. For by filling a narrow capillary, which was coated by a thin liquid layer, the surface energy of the liquid will disappear and be converted into heat. From the quantity of heat liberated we can calculate the area of liquid surface which has disappeared, provided that the surface tension of the liquid is known.

From the figure the amount of heat which is due to the final rise of $\frac{dQ}{dA}$ can be estimated, although only approximately. This represents, for instance with ether at 10°C., a quantity of heat of about 0.5 calorie. The free surface energy per square centimeter of surface is for ether at 10°C. about 18 $\frac{ergs}{cm^2}$. Consequently the liquid surface must have been about 116 square meters. At −7°C. the amount of heat due to the rise of $\frac{dQ}{dA}$ is greater (see figure 11); also the free surface energy is then greater.

That exactly the same surface for the liquid should be found as we calculated for the charcoal of Lamb and Coolidge, was not to be expected. In the first place, the charcoal worked with was of

a different kind; in the second place, the liquid surface must always be smaller than that of the charcoal, since the roughnesses of the surface and the very small cavities are filled sooner.

The fact that the values calculated for the liquid surface and for the charcoal surface are of the same order proves that the capillaries of the charcoal used do not differ much in diameter, and that they are first covered regularly with a liquid layer. Just before saturation a very small quantity of liquid will suffice to fill the pores entirely.

The maximum surface, which one normal cubic centimeter of ether can have at 10°C. as liquid, is 16.3 square meters (this is the total surface of both sides of the monomolecular layer). This is therefore also the largest surface, which can disappear by condensation of one normal cubic centimeter of ether, in case it finds liquid molecules on both sides. The heat which is liberated in that case is about 0.07 calorie per normal cubic centimeter, which therefore is the largest amount which the surface energy can attribute to $\frac{dQ}{dA}$ for ether at 10°C.

If we now look at the curves calculated for n-pentane from Goldmann and Polanyi's isotherms, we see here exactly the same thing as with ether. At 10°C. the filling of the second layer begins at a smaller value of A than at -7°C.; therefore at the lower temperature the real heat of adsorption had fallen more, before the rise of $\frac{dU}{dA}$ set in. The filling of the capillaries makes itself obvious here by the steep rise of $\frac{dQ}{dA}$. The curves are however not known up to saturation; neither do we know the surface tension of n-pentane. Consequently the liquid surface cannot be calculated here.

We now can draw for both temperatures the "real heat of adsorption" (see figure 14). These are smooth curves, which in the beginning fall very steeply, later on more slowly; they do not coincide for two temperatures, although the difference is not great.

In the systems dealt with heretofore, the kink in the $\dfrac{dU}{dA}$ curve, where this curve rises from RT to the heat of condensation, lies at a concentration too small to be noticed. However it appears again in the SO_2 line from Polanyi and Welke (figure 10) where the rise after $A = 0.33$ cc. shows the condensation into liquid.

The NH_3 line determined by Titoff at 0°C. (figure 2) begins to rise at $A = \pm90$ normal cubic centimeters, which indicates that
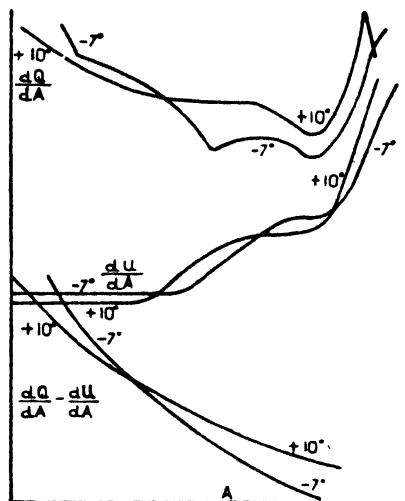
FIG. 14. n-PENTANE ON CHARCOAL AT 10°C. AND −7°C.

Heat of adsorption, heat of compression and real heat of adsorption.

The value of $\dfrac{dQ}{dA}$ of the abscissa is 0.07 calorie.

the second layer is built up there. (If it meant that the capillaries were filled, the rise would be steeper and much nearer to saturation.) The surface, which is covered by 90 normal cubic centimeters of NH_3 in a monomolecular layer, is 306 square meters. The charcoal of Titoff therefore has a greater specific surface than that of Lamb and Coolidge.

Titoff is of the opinion that the rise of $\dfrac{dQ}{dA}$ is due to the formation of liquid, and concludes from the difference between the

value of the minimum and the higher values at subsequent volumes, what part of the adsorbed quantity condenses. This cannot be correct, for should 90 normal cubic centimeters be present on the charcoal in non-fluid condition, they would take up a volume of at least 21 cc. per gram of charcoal (the saturated vapor-pressure of NH_3 at 0°C. is 4.3 atmospheres). This is impossible, certainly for the compact cocoanut charcoal used by Titoff.

The argument of Tryhorn and Wyatt, who measured the rate of adsorption of saturated vapors on cocoanut charcoal, is erroneous for the same reason. They hung one gram of charcoal above the surface of a pure liquid at 20°C., and determined the increase in the weight of the charcoal with time. They found that $\frac{dA}{dt}$ (t = time) against t always gave a curve with a kink, and ascribed this kink to the sudden formation of a liquid layer on the charcoal. The difference in concentration between the surface of the pure liquid and that of the charcoal covered with a small layer of liquid would then be so small, that the rate of adsorption would also be very small. In most curves the kink is situated in the neighborhood of 2/3 to 5/6 of the saturation-quantity, for instance for ethyl alcohol at 53.6 normal cubic centimeters adsorbed. The assumption that a liquid layer is formed suddenly when this large amount has been adsorbed, is evidently absurd. The cause of the apparent discontinuity of the $\frac{dA}{dt}$ against t curve may probably be found in the form of the isotherm, for the rate of adsorption is proportional to the difference in pressure above the pure liquid and above the charcoal. At smaller values of A, p is so small that, compared with the saturated pressure, it may be neglected, but at $A = \pm 2/3$ of the saturation-quantity, p is increasing strongly. There is apparently a sudden change in the pressure, but a liquid layer had previously been formed on the charcoal.

It is true that above the critical temperature of the adsorbed substance the heat of condensation disappears, but not the heat of compression, which remains equal to RT, except for the devia-

tions from the laws for ideal gases. Whether more layers will form on the charcoal cannot be said with certainty; probably this will be the case at a lower temperature.

Of course it is not correct to ascribe each rise in a $\dfrac{dQ}{dA}$ curve to a heat of compression. When we recall the curves which have been found for O_2 on charcoal and for H_2 on nickel and on copper catalysts (figure 6), we understand that the cause of the rise can be quite different. The curve for O_2 rises from $A = 0$ to a value eleven times larger than its initial value. However, there is here no longer any question of real adsorption, but chemical interaction with the charcoal takes place. This is evident from the fact that in case of desorption only part of the oxygen can be recovered, and that when evacuating at a higher temperature, CO and CO_2 are set free (McLean). The quantities which are first adsorbed occupy the most active places of the surface and should therefore give the greatest heat effect, provided that no heat had been used to dissociate the O_2 molecule.

Each oxygen atom then combines with the charcoal to form one or more complexes, Garner and McKie distinguish three complexes which are possible, viz.:
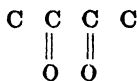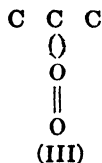
```
C  C  C  C        C  C  C          C  C  C
‖  ‖                ⟋⟍              ()
O  O              O——O            O
                                   ‖
                                   O

   (I)              (II)            (III)
```

(I) gives CO with desorption, (II) gives CO_2 and (III) gives unchanged O_2.

When evacuating at a higher temperature charcoal which had previously adsorbed O_2, it appears that the maximum evolution of CO_2 lies between 300°C. and 400°C., that of CO between 600°C. and 700°C. (Rhead and Wheeler). Over a large range of temperatures CO and CO_2 both appear; the surface of the charcoal will therefore always be dissimilar. The supposition is that at very small concentrations complex (I) is formed. This implies a complete dissociation of the O_2 molecule. Only the most

active spots of the charcoal are able to cause such a dissociation; the liberated heat is therefore small. At larger values of A, complex (II) is formed; here the connection between the oxygen atoms is loosened but not broken; the liberated heat is great. If A becomes still larger we get complex (III), real adsorption, whereby the O_2 molecule remains intact; the liberated heat is here of the same order as the heat of adsorption of other gases.[4] For H_2 on catalysts the situation is essentially the same. We have no real adsorption here either, but chemical action interferes. At the most active points on the surface the hydrogen will be bound atomically, and heat is used for the dissociation of the H_2 molecule.

The third case of a rising $\dfrac{dQ}{dA}$ curve was that of H_2O on charcoal. Here the heat of adsorption has a smaller value than the heat of condensation. This might be due to the fact that the heat of compression for H_2O at $0°C$. is negative, at least for the first 200 atmospheres. The condensation of water vapor into a compressed liquid therefore gives a smaller heat than the normal heat of condensation; at higher pressures the difference becomes smaller.

However, the behavior of H_2O with regard to charcoal, which in many respects is different from that of the organic liquids, may also be considered from another standpoint, which at the same time shows us a quite different side of the problem of adsorption.

In case the heat of adsorption of a substance is smaller than its heat of condensation, the substance is adsorbed more at a higher temperature and at the same relative pressure. (By relative pressure we mean the pressure p, divided by the saturated vapor-pressure p_s). For,

$$\frac{dQ}{dA} = RT^2 \frac{d \ln p}{dT} = RT^2 \frac{d \ln \dfrac{p}{p_s}}{dT} + RT^2 \frac{d \ln p_s}{dT}.$$

[4] In a recent paper Marshall and Bramston Cook publish heats of adsorption for O_2 on charcoal at $0°C$; here the initial values are very high. The course of the curve they find is quite different from that of Garner and McKie, although at greater pressures the values coincide. Especially at very small concentrations do different kinds of charcoal behave quite differently.

The last term is the heat of evaporation. When this is greater

than $\dfrac{dQ}{dA}$, then $\dfrac{d\ln\dfrac{p}{p_s}}{dT}$ must be negative. At a higher T, $\dfrac{p}{p_s}$ is

smaller at the same A; and at the same $\dfrac{p}{p_s}$, A is consequently greater. The shape of the isotherms is different here from those in the case of the organic liquids.

Coolidge (14) has determined isotherms of water on charcoals with different ash contents and has found that the influence of the ash content was great, especially at small concentrations.
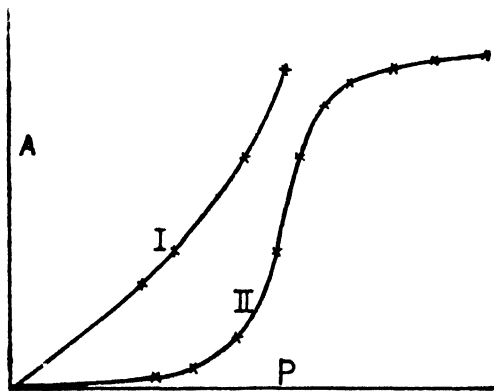
FIG. 15. ISOTHERMS OF H_2O ON CHARCOAL AT 0°C.
I—cocoanut charcoal; II—sugar charcoal

The isotherms at 0°C. on cocoanut charcoal, which contains rather many inorganic impurities, and on sugar charcoal, which does not contain them, are shown in figure 15. At small values of p, the course of the curves is quite different. (An analogous diagram has been found by Trouton and Miss Poole for the isotherms of water on glass wool, which has been dried in various ways.) With pure sugar charcoal hardly anything is adsorbed between $p = 0$ and $p = 1.5$ mm. Hg; at higher pressures, A at once increases steeply. The equilibria were all reversible; the same p was found whether working at decreasing or at increasing pressure (with cocoanut charcoal such was not the case). The

shape of the isotherm of H_2O on sugar charcoal is indeed quite different from that of an organic liquid, where in the stretch of pressures $p = 0$ up to $p = 1.5$ mm. Hg, more than half of the quantity necessary for saturation is adsorbed.

This difference is explicable, because the adhesion between charcoal and an organic non-polar liquid is so much greater than that between charcoal and water. Charcoal is wetted spontaneously and completely by an organic liquid, and the angle of contact is $0°$; with water the wetting is not complete, and the contact angle is between $0°$ and $180°$. Bartell and Osterhof have worked out a very ingenious method to determine quantitatively the adhesion tension even when the contact angle is $0°$. They found that the work of cohesion of benzene is much smaller than the work of adhesion with charcoal; for water it is just the opposite.

Therefore work is required to replace a water-water interface by a charcoal-water interface, and consequently the heat of condensation of water on a surface of charcoal must be smaller than that on a water surface. If the surface of the charcoal is covered, we once more get the normal heat of condensation.

This consideration enables us to calculate the specific surface of the charcoal, for instance in the system H_2O on charcoal, according to Keyes. Considering the point where the normal heat of condensation is reached as the beginning of a second layer, we calculate for the surface of the charcoal 60 square meters per gram, i.e. a somewhat smaller value than that derived from Keyes' diagrams for ether on charcoal.

The course of the isotherms on various kinds of charcoal can now be explained too. Large ash contents of the charcoal, i.e. many inorganic impurities, make the work of adhesion for water greater, and therefore the adsorption at small pressures will also be greater. With increasing temperature, the cohesion decreases more than the adhesion. (At the critical point there is no longer any surface tension, but there is still adsorption.) Consequently at small pressures the isotherm for higher temperature is situated above that for lower temperature, and at the same relative pressure A increases with increase in T.

Bartell and Osterhof assume that the inner pressure of a liquid

is a function of the surface tension, and that the relation between the pressure in the adsorption layer and the inner pressure of the liquid is the same as that between the work of adhesion and that of cohesion. Therefore the pressure of adsorbed H_2O will be smaller than the normal inner pressure, while the opposite is true with organic liquids.

Coolidge (14) found the same behavior as that of H_2O for the adsorption of Hg vapor on charcoal. With nitrogen on charcoal at 15°C. and at very small pressures, Rowe found an analogous behavior, but the curvature of the isotherms was smaller in this case; at −183°C., however, the curve ran normally. As we are here above the critical point, the comparison with the heat of condensation is impossible and the terms "work of adhesion" and "cohesion" have lost their usual meaning. The fact, however, that $\left(\dfrac{dA}{dp}\right)_T$ increases when the charcoal has already condensed some nitrogen on its surface, proves that the attraction of the charcoal for a nitrogen molecule is smaller than the mutual attraction between two nitrogen molecules (at the same distance). Figure 9 for the calculated heat of adsorption of nitrogen shows that at different temperatures the curves first rise and then run nearly horizontally; near 0°C., however, the heat of adsorption has the usual course, as appears from isotherms of Titoff and Miss Homfray. Evidently these relations are very dependent on the temperature.

The behavior of H_2O, of Hg vapor and of N_2 with charcoal emphasizes the chemical forces between adsorbent and adsorptive, just as well as does the adsorption of O_2 on charcoal and of H_2 on metals. In the latter cases the chemical forces are dominating; in the first cases they are failing.

These results contradict the idea that the adsorption is not specific; in the case of O_2 we can still say that we have nothing to do any more with real adsorption, but with H_2O and N_2 this is surely the case. The part played by the chemical forces at adsorption would be much clearer, if most investigators had not experimented exclusively with charcoal, and especially with a kind having a high ash content.

For the adsorption of H_2O the influence of such inorganic impurities has already appeared clearly; for SO_2 and NH_3 it will also make a difference what kind of charcoal is used. As for the adsorption of organic liquids on charcoal, the first layer will probably be orientated in such a way that in the first instance we shall have always to do with the forces between the charcoal and the carbon atoms of the liquid layer. Great divergencies may consequently not be expected there, and the conclusion as to whether adsorption is specific or not may not be drawn from the results.

V. CONCLUSIONS FROM THE HEAT OF ADSORPTION AS TO SOME THEORIES ABOUT GAS ADSORPTION

The heat of adsorption is often used to calculate other quantities, chiefly the specific volume of a gas in the adsorbed condition.

In accordance with the principle of Maxwell-Boltzmann, the entropy of a state is proportional to the logarithm of its probability. For the difference of entropy between free and adsorbed gas the heat of adsorption q (per gram-mol) is taken. The probabilities of the two states are assumed to be proportional to the molecular volumes V_V (in free) and V_A (in adsorbed condition)

$$\frac{V_V}{V_A} = e^{\frac{q}{RT}}$$

From this we shall try to calculate V_A in some cases:

Case I. For CO_2 at 0°C., Titoff finds, at $p = 2.4$ mm. Hg, the value of q to be $\frac{dQ}{dA} \times 22,400 = 7773$ calories. $V_V = \frac{760}{7.4} \times 22400$ cc. Then V_V becomes $= 4.39$ cc. The molecular liquid-volume at 0°C. for CO_2 is $\pm$ 48.9 cc.

Case II. For NH_3 at 0°C. Titoff finds, at $p = 2.6$ mm. Hg, the value of q to be $0.501 \times 22,400$ calories. V_A then becomes 0.0067 cc. The molecular liquid-volume at 0°C. for NH_3 is $\pm$ 27 cc.

Case III. For benzene at 0°C., Lamb and Coolidge find at $p = 2$ mm. Hg, the value of q to be $0.75 \times 22,400$ calories. V_A then becomes 0.00004 cc. The molecular liquid-volume of benzene at 0°C. is $\pm$ 88.5 cc.

From these examples it appears that no real meaning may be attributed to the volumes found, which are so much smaller than the liquid-volumes. The compressibility of liquids is small; therefore the specific volume even at high pressures cannot differ much from that at one atmosphere.

Polanyi and Welke, who have determined the adsorption of SO_2 on charcoal at very small concentrations, calculated the density in the adsorption layer according to Maxwell-Boltzmann, and also found impossible values. They therefore introduced the term "apparent density," and determined the change of this quantity with increasing concentration. If they applied the formula to a vapor-liquid equilibrium, when q is the heat of evaporation and V_V the specific volume of the saturated vapor, it appeared that the apparent density of a pure liquid was $\pm 3 \times$ the real density.

Jacquet and Hückel write the formula of Maxwell-Boltzmann:

$$\frac{A V_V}{r} = e^{\frac{q}{RT}}$$

in which V is the adsorption volume of one gram of charcoal. The density of the gas is $n = \dfrac{1}{V_V}$, and consequently

$$\frac{A}{n} = V e^{\frac{q}{RT}}.$$

If $\ln \dfrac{A}{n}$ (at constant n) is drawn against $\dfrac{1}{T}$, a straight line must be found, from which $\dfrac{q}{R}$ and $\ln V$ can easily be found graphically.

For SO_2 and NH_3 the curves appeared not to be straight, and therefore the results are inaccurate; but for various gases Hückel obtains in this manner values for V and q. These q values are smaller than those determined directly. Hückel finds for N_2 3200 calories (± 4500 calories is determined); for CO_2, 5560 calories (6750 calories is determined) etc. For the adsorption volume per gram of charcoal he finds ± 0.05 cc.

That the deviations between the values found and those calculated according to Maxwell-Boltzmann are not as great here as in the calculation of the specific volume of the liquid layer, is due to the form of the equation, but does not prove anything at all for its validity.

Iliin thinks it possible to determine the surface of an adsorbent by means of the e-formula. If r be the thickness of the adsorption layer and S the surface of one gram of adsorbent, then

$$\frac{A}{Sr} = \frac{1}{V_V} e^{\frac{q}{RT}}.$$

At the same pressure, temperature and heat of adsorption the quantity adsorbed per square centimeter of surface must always be equal (as Iliin takes account only of monomolecular layers, r is always the same for the same adsorptive). The conclusion is that adsorption is not specific at all! If we know q and A for one adsorptive at the same p and T on two adsorbents, of which one has a known surface, S can be calculated for the other adsorbent. This Iliin does for charcoal.

Without using an adsorbent with a known surface, Iliin's conclusions can easily be tested. If we have two adsorbents with specific surfaces S_1 and S_2, on which A_1 and A_2 have been adsorbed per gram at the same p and T, whereby the heats of adsorption are q_1 and q_2 then:

$$\frac{\frac{A_1}{S_1}}{\frac{A_2}{S_2}} = \frac{e^{\frac{q_1}{RT}}}{e^{\frac{q_2}{RT}}} \quad \text{or} \quad \frac{S_2}{S_1} = \frac{A_2}{A_1} e^{\frac{q_1 - q_2}{RT}}$$

Now $\frac{S_2}{S_1}$ must be independent of the adsorptive with which the relation is determined, as otherwise there would still be a question of a specific effect. However $\frac{S_2}{S_1}$ is not constant at all. In calculating from Chappuis' measurements the relation between the specific surface of the charcoal and that of the meerschaum used, with SO_2 as adsorptive, we find, if S_2 is the charcoal surface, that

$\dfrac{S_2}{S_1}$ = 3.08 (calculated at 0°C. and 30 mm. Hg).   With NH$_3$ as

adsorptive at the same T and p, $\dfrac{S_2}{S_1}$ becomes 169.   In other cases

the agreement is just as bad.

It is generally known that the principle of Maxwell-Boltzmann does not exactly represent the facts in many cases, especially when we have to do with weak bonds between atoms or molecules, as, for instance, with the specific heat of polyatomic gases. In adsorption we often have to do with weak bonds and chemical forces between the molecules of the adsorbent and the adsorptive; the more these specific influences prevail, the greater the error made when using the e-formula.   With the systems studied by Kälberer and Mark (for instance, argon on silicic acid), the formula gives useful results, but there the requirement that the number of degrees of freedom of the molecule in free and adsorbed condition must be equal, is fulfilled (Sementschenko).   If this is not the case, the known smooth curve of Maxwell for the distribution of energy can not be applied, but must be replaced by the stepped figure, as calculated by means of the quantum theory.

A somewhat exaggerated metaphor enables us to explain why we always find too small a value, when calculating the specific volume in adsorbed condition by the e-formula.   The force exerted by the charcoal diminishes very markedly with increase in the distance from the surface.   If we suppose that the adsorbed molecules are situated on the charcoal as are pins on a pin-cushion, the field at the point of the pin determines the adsorption and the heat of adsorption.   This value of q is used in the formula, and therefore we calculate in reality the volume of the pin-point. About the volume of the pins themselves, however, we cannot conclude anything; a conception such as Polanyi's "apparent density" is therefore of no value.

The potential theory also tries to explain the adsorption from a purely physical standpoint.   According to this theory, developed for gases below the critical temperature by Polanyi (later on also by Berenyi, Lowry and Olmstead and others), the potential ϵ of a

point is determined only by the distance from the adsorbing sur-
face, and is independent of whether the interjacent space is filled
or not.   This distance being determined by the quantity already
adsorbed, ϵ depends exclusively on A; this relation is called the
characteristic function.   Polanyi, assuming that the equation of
state is applicable, finds

$$\epsilon = RT \ln \frac{p_s}{p_A},$$

in which p_s is the saturated vapor-pressure.   For the heat of
adsorption

$$\epsilon = q + T \frac{d\epsilon}{dT}$$

holds, but according to Polanyi $\frac{d\epsilon}{dT} = 0$ over a large range of
temperatures above 0°K, therefore $\epsilon = q$, and the net heat of
adsorption, drawn against A, gives the characteristic function.
Polanyi and his collaborators do not calculate the latter from
calorimetric data, but from isotherms, and they then find curves,
which indeed fall in the beginning but afterwards run rather flat.

Hückel has calculated that this cannot be correct, since a
potential which depends only on the distance from the surface
must fall abruptly to 0.   The curves which we found for the heat
of adsorption show clearly that this opinion of Polanyi cannot be
correct, for then the potential would increase again with an in-
crease of the distance from the surface.

If $\frac{d\epsilon}{dT} = 0$, then $\frac{dQ}{dT}$ must be 0.   This is not correct either,
although $\frac{dQ}{dT}$ is sometimes small.   The potential and the heat of
adsorption cannot be identified therefore, and the mutual action
of the molecules of the adsorptive contributes considerably to
the heat of adsorption.

Goldmann and Polanyi have tried to improve the theory with-
out throwing overboard the good results obtained in many cases.
They assume that the adsorption layer is monomolecular at small
concentrations, and that the difference of the potential arises from

the roughness of the charcoal surface. Around the most active spots isles of liquid are first formed, and the potential depends exclusively on the adsorbed volume. Goldmann transforms the isotherms to affinity curves, i.e. he draws the affinity F against A

$$F = RT \ln \frac{p_s}{p_A}$$

The different curves do not coincide, but run very close to each other. Although the potential is independent of T, according to Goldmann and Polanyi, the affinity indeed changes with T at constant A, owing to the dilatation of the adsorptive. In general the following holds:

$$F = q + T \frac{dF_A}{dT} = q - T \left(\frac{dF_A}{dA}\right)_T \left(\frac{dA}{dT}\right)_F.$$

The heat of compression of a liquid is proportional to the pressure and to the dilatation of the liquid. Now $-\left(\dfrac{dF_A}{dA}\right)_T$ represents the gradient of the potential at right angles on the equipotential surface F_A, and is therefore a measure of the force with which the liquid is compressed, and $\left(\dfrac{dA}{dT}\right)_F$ is proportional to the dilatation of the liquid. The second term to the right in the equation above represents the heat of compression of the adsorbed liquid owing to the quantity just admitted, and the affinity is the difference between the heat of adsorption and the heat of compression. The curves which we have drawn in figures 13 and 14 for the "real" heat of adsorption, therefore represent the same as Goldmann's affinity. This "real" heat of adsorption however arises not only from the direct influence of the adsorbing surface, but also from the attractive power exercised by the first layer on newly admitted molecules. We may not say therefore that the affinity on a certain point is independent of the fact whether the space between the adsorbent and that point is filled or not. Moreover, it is not correct that the potential is independent of the temperature and that the reason why the affinity curves for different values of T do not coincide must be sought only in the

dilatation of the liquid.   Goldmann himself finds that this dilatation is different, when calculated from affinity curves, or when determined experimentally.   The difference is considerable especially at small concentrations.   If Goldmann had also determined isotherms of water on pure charcoal, he would have found, for instance between 10°C. and 20°C. a shrinking of the liquid at increasing temperature instead of a dilatation.   For with water, A increases with T at constant $\dfrac{p_s}{p_A}$; consequently at the same A, F is greater at higher T.

This shows clearly the one-sidedness of the potential theory. Its hypotheses are approximations, which however in many cases can represent the facts with sufficient accuracy, at least beneath the critical temperature and at higher concentrations, where chemical forces are of less influence.

According to Patrick and his collaborators Greider, McGavack, Davidheiser and Long, adsorption is based upon condensation of liquid in the pores of the adsorbent.   Indeed, the vapor-pressure over a highly curved surface is smaller than above a plane one. The relation between the radius of curvature of the surface and the vapor-pressure above it is expressed in Lord Kelvin's equation.

If vapor is admitted to an adsorbent, for which Patrick usually takes silica gel, at small values of p the narrowest pores will be the first to be filled with liquid and then gradually wider ones will fill.   For the same gel, the relative vapor-pressure $\dfrac{p}{p_s}$, according to Patrick, depends only on the volume already filled.   (Just as in the case of Polanyi's work, the molecular liquid-volume is of great importance here.)   From the knowledge of one isotherm and the change of density of the liquid with the temperature, it is possible to calculate the other isotherms.

However, the adsorbed liquid-volume at constant relative pressure appeared to be smaller at higher temperature, except for $\dfrac{p}{p_s} = 1$; there the liquid-volume is about constant.   According to Patrick the liquid is submitted to a negative pressure, in that

the surface tension will try to make the interface liquid-vapor as small as possible by filling the capillaries as far as possible. The density is smaller than the normal value and approaches the latter as $\frac{p}{p_s}$ approaches 1.

Lord Kelvin's equation not being applicable to radii of curvature of molecular dimensions, Patrick used an empirical formula

$$V = K \left(\frac{p \, \sigma}{p_s} \right)^{\frac{1}{n}}.$$

in which V represents the liquid-volume, σ the surface tension and K and $\frac{1}{n}$ are constants. The formula corresponds to the facts fairly well except at small relative vapor-pressures and near the critical temperature. The formula does not show, however, that the influence of σ on V must be different at different relative vapor-pressures and that at $\frac{p}{p_s} = 1$, V is constant. Since V becomes smaller with increasing T at the same $\frac{p}{p_s}$, multiplication by a quantity, which decreases at higher temperature, will improve the agreement. Gregg (32) therefore tried $\frac{1}{T}$ instead of the surface tension, used by Patrick, and found that, in general, this was more satisfactory.

Patrick explains the decrease in V at constant $\frac{p}{p_s}$ with higher T from the abnormal density of the liquid. However, this argument is completely refuted by Coolidge (13). He pointed out that V must change with T, as V depends on σ and on the density of the liquid and the dependencies of those quantities on T do not neutralize each other.

It is not logical to try to attribute adsorption at small concentrations to capillary condensation. This appears only when the surface is completely wetted by the liquid, i.e. when the cohesion is much smaller than the adhesion. If the cohesion is greater,

the meniscus is lower in a capillary than in a wide tube (Hg in glass) and the vapor-pressure over the curved surface is greater than the normal one. When the adhesion is greater, Patrick explains everything by means of cohesion, or what comes to the same thing, by means of surface tension.

As long as the influence of the surface is mainly a direct one, we have to do with adsorption. We speak of capillary condensation only when, owing to the form of the surface, an arriving molecule comes into the field of force of more adsorbed molecules than it would in the case of a plane surface, and is then held by them. The influence of the surface is then entirely indirect.

This is also the case, when the electric conditions of the surface cause an induced cohesion. De Boer has given a beautiful example of this kind. He determined the quantity of iodine adsorbed at different pressures by a small layer of calcium fluoride on a glass surface. The surface of the CaF_2 layer being larger than that of the glass covered by it, the thickness of the adsorption layer cannot be calculated with absolute accuracy from the quantity adsorbed; probably it has the thickness of many molecules. When the iodine vapor was saturated, a layer of iodine could be perceived on the uncovered glass.

The explanation for the thickness of the layer is that the first layer of iodine is bound by the field of force of the calcium and fluoride ions; consequently the atoms of iodine become dipoles, which in their turn can adsorb a next layer. As a matter of fact the polarizing effect becomes weaker in following layers. This induced cohesion, which is important in many cases, cannot be separated from pure adsorption.

Moreover, the limit between capillary condensation and adsorption is also very difficult, if not impossible, to stipulate. In fact, we ought to unroll the curved surface and see whether the same quantity remained on it; if so, we have to do with adsorption.

In section IV we have seen that sometimes one can conclude from the curves for the heat of adsorption, where the capillaries are filled. In the cases discussed above (ether and pentane on charcoal), the adhesion was great with regard to the cohesion, so

that each molecule was drawn as near as possible to the surface of the charcoal. With the cocoanut charcoal of Lamb and Coolidge it appeared that at about $A = 23$ ncc. the second layer began; at saturation, about 100 normal cubic centimeters were adsorbed; the thickness of the layer will therefore be four to five molecules, i.e. the average diameter of a capillary is that of nine ether molecules. It is now evident from the curve for the heat of adsorption, that the charcoal surface is covered almost entirely and regularly on all sides with a layer which has the thickness of four molecules, and only when the pressure is almost equal to that of the saturated vapor does the last layer come into the capillary. In such cases one is not justified in making a distinction between capillary condensation and adsorption.

However, this may be important when the pores of the adsorbent differ very much in width, or when the adhesion is not as great in proportion to the cohesion as in the cases above. Then at increasing concentration pores will be filled gradually and the surface energy will be gradually liberated as heat, i.e. the heat of adsorption will not show a steep rise near saturation and will possibly not rise at all (compare for instance the curve for SO_2 on blood charcoal, figure 5). Therefore the influence not only of the inner volume, but of the whole structure of the adsorbent appears to be great.

Langmuir alone calls adsorption a chemical phenomenon; crystallization and evaporation also belong, according to his opinion, to this category. Langmuir holds the unsaturated valences of the surface atoms responsible for the adsorption. On the surface a number of equivalent spaces, "elementary spaces" are available, which, in the most simple case, can contain one molecule of the adsorptive each. Langmuir works with adsorbents of known surface and considers the equilibrium from the standpoint, of the kinetic gas theory: the number of molecules leaving the surface per unit of time is equal to the number clinging upon it. The number of molecules which collide depends on the pressure, the temperature and the molecular weight of the substance; the number which cling depends on the probability

of adhesion and on the occupation of the surface; the number which evaporate also depends on the occupation and on the rate of evaporation. From this Langmuir comes to the formula for the isotherm $A = \dfrac{abp}{1 + bp}$, in which a is a constant, depending on the number of elementary spaces per unit area, and b a constant, depending on the probability of adhesion and the rate of evaporation from a fully occupied surface. Then

$$\frac{p}{A} = \frac{p}{a} + \frac{1}{ab}.$$

$\dfrac{p}{A}$ drawn against p must give a straight line, from which a and b can be found graphically. If Langmuir draws his determinations (at 90°K and 155°K) in this way, the curve is indeed straight, if the pressures are not situated far from each other (the greatest pressure applied by him is 172 bar = 0.13 mm. Hg). Moreover, Langmuir finds, in two or three control series, other constants in his formula, so that, when calculating A at determined p, using the various constants, we find values which differ by 30 per cent. If Langmuir calculates from the constants found the number of elementary spaces per unit area, he finds at 90°K for mica sometimes 9×10^{13}, sometimes six times as much. For glass the differences are still greater.

Langmuir himself disregards the quantity adsorbed in a blank experiment (possibly on the wall of the apparatus), which amounts to 10 to 30 per cent of the quantity found in the real experiment, since this amount does not surpass the experimental error. The cause of these large experimental errors and the poor agreement between control determinations is in the first place due to fluctuations in the temperature (against which no precautions were taken), and further to the inaccuracy of A, which was calculated from a small difference of pressure in a large volume.

The accuracy of Langmuir's experiments is not greater than up to 30 per cent; probably it is hardly possible to obtain a greater accuracy at these very small pressures, but the question arises as to whether such determinations are adequate to prove a theory.

The cases where the curve of $\dfrac{p}{A}$ against p is not at all straight, Langmuir ascribes to the existence of various kinds of places on the surface. For this case he derives a complicated formula, which contains two constants for each kind of place. Also the possibility that an elementary space can contain more than one molecule, is considered; this also leads to a formula with many constants. In this manner indeed values calculated and found can be brought to agreement, but the practical usefulness of such a formula is then strongly reduced.

Zeise finds that for his determinations on glass the formula must be $A = \sqrt{\dfrac{abp}{1+bp}}$, which means that two spots of adsorption hold one gas molecule. However, he also uses in control determinations other constants, which differ much. Zeise (as well as Langmuir) thinks the theory also applicable on charcoal as an adsorbent and he calculates data of Miss Homfray, Titoff and Richardson with Langmuir's formula, and finds the agreement very satisfactory.

Polanyi (71) observes that the way in which the constants depend on the temperature should be quite different from what it really is, if the constants had the meaning ascribed to them by Langmuir. He is of the opinion that the assumption that the number of elementary spaces per square centimeter of surface varies strongly with the temperature, is unjustified.

Probably from the agreement with the facts, resulting from Langmuir's formula of adsorption on charcoal and at higher pressures, we may conclude that the formula has a great flexibility and therefore is able to represent the facts fairly well, even in the cases where the hypotheses of Langmuir seem to be not quite correct.

Originally Langmuir assumed that the adsorbed molecules had no influence on each other. Later on (51) he reversed his opinion on this, and he agrees with Clausing when the latter states "that there is more work required to have a molecule (of a metal vapor) evaporated, when it is situated quite close to another one on the glass wall, than if it is present there individually. The

rate of evaporation is greatest for isolated molecules." The difference will be greater in proportion as the cohesion is greater and the adhesion smaller. Only when the adhesion is greatest, may one neglect the influence of the adsorbed molecules on each other at small pressures.

The fact that the thickness of the layer is no more than that of one molecule at the small pressure at which Langmuir worked, does not mean anything as to the condition at greater pressures. The quantities of gas obtained by Langmuir when evacuating his adsorbents, are often much too large for a monomolecular liquid layer on the known surface. Here we must draw attention to the fact that according to experiments made by Frazer, Patrick and Smith the surface of glass is usually not smooth. Glass which has been in contact with a trace of water is covered with a layer of silica gel, which has a large inner surface so that the active surface of glass is unknown in most cases.

Langmuir does not prove that the adsorption layer is monomolecular, but he assumes that only the quantity present in the first layer is bound by adsorption. Against this hypothesis many objections can be raised.

Reichenstein (74) has come to the same form for the isotherm as found by Langmuir, but in a quite different way. He considers the adsorption volume as if it were a solvent between two other solvents (solid and gas). The relation between the concentrations depends on Henry's law and on the distribution coefficients. According to Reichenstein's "displacement principle," the sum of the concentrations of all substances in the adsorption layer is constant. In this the concentration of the adsorbent is also included, i.e. a certain number of molecules of the solid which cause adsorption.

If the concentration of one gas in the adsorption space is expressed in terms of the other concentrations with the aid of the distribution coefficients and the constant sum in question, the formula obtained in the case of one adsorptive has the same form as Langmuir's isotherm. The theory cannot be right however, as it has appeared from various experiments that at adsorption of a mixture of two gases, the sum of the quantities

adsorbed is greater than the quantity of one of the two gases, which would be adsorbed if it were present separately with the same pressure (Bergter and others). Therefore the concentration of the solid in the adsorption volume must be smaller than in the case of only one gas being present, i.e. fewer molecules of the adsorbent participate in the adsorption. We meet with a similar case when only one gas is adsorbed at increasing concentrations; the more there is being adsorbed, the less adsorbent should participate. This is inconceivable. In fact, Henry's law is applicable only at temperatures far above the critical one, and at not too great pressures. In such cases all relations are much simpler; here it is possible (Lorenz and Landé) to apply the law of the corresponding states to the adsorption, and to express the adsorption of various gases on the same adsorbent in one diagram, reduced to critical quantities.

What we have said above leads to this unsatisfactory conclusion; that there is neither an empirical equation nor a theoretical one which can account for all the data which experiments have given us. Everyone will be inclined to put this question: What is, in your opinion, the right equation for the adsorption isotherm —the empirical equation of Freundlich, or the theoretical one of Langmuir, or another one? We are obliged to reply that we cannot give a general answer to that question, since none of the experimental equations and none of the theoretical equations, given up to now, is correct.

The empirical equation of Freundlich $A = \alpha p^{\frac{1}{n}}$ cannot express saturation; moreover the initial slope is always infinite, which in reality is the case only at low temperatures and great adhesion.

According to Langmuir $\frac{p}{A}$ drawn against p must give a straight line, consequently $\dfrac{d\,\frac{p}{A}}{dp}$ must be constant. According to Freundlich this is the same as

$$\frac{1}{A} - \frac{p}{A^2}\left(\frac{1}{n}\,\alpha\,p^{\frac{1}{n}-1}\right) = \frac{1}{A}\left(1 - \frac{1}{n}\right).$$

This must be constant, therefore $1 - \dfrac{1}{n}$ must increase in proportion to the increase of A. Saturation can indeed be expressed by Langmuir's isotherm.

According as $\dfrac{1}{n} = \dfrac{d\ln A}{d\ln p}$ remains rather constant, or decreases at greater concentrations, either the formula of Freundlich or that of Langmuir is most fit for use. Titoff and many others always give the values for $\dfrac{1}{n}$, calculated from their figures. From this the insufficiency of both equations is evident at a glance. For N_2 at $-79°C.$, $\dfrac{1}{n}$ falls from 0.74 to 0.40; on the contrary at $+151.5°C.$, $\dfrac{1}{n}$ increases from 0.89 to 1.02. For NH_3 at $30°C.$, $\dfrac{1}{n}$ first increases with rising p from 0.42 to 0.79, and then falls again to 0.40.

Williams recommends as isotherm $\ln\dfrac{A}{p} = B_0 - B_1 A$ (B_0 and B_1 are constants). The derivation is not at all convincing, but at small concentrations (up to ± 30 per cent of the value of saturation) the formula represents the facts fairly well.

The formula of Arrhenius

$$K\frac{dA}{dp} = \frac{C - A}{A}$$

(K is a constant and C is the saturation-quantity) is useful, especially at great concentrations and near saturation. This equation is analogous to that used by Schmidt for adsorption from solutions.

All these formulas are equally adequate; each has a domain in which it is useful, but none of them is able to express a complete isotherm at lower temperatures.

This is not at all strange, because many different items are

important for the various parts of the isotherm. The initial slope and the beginning of an isotherm are determined by:

1. The chemical forces between adsorbent and adsorptive,

2. The temperature and the duration of the activating and outgassing of the adsorbent,

3. The specific surface of the adsorbent,

4. The condensability of the adsorptive,

5. The electric qualities of the adsorptive (the di-electric constant, whether the adsorptive molecule is a dipole, etc.).

Moreover, at greater pressures, the following are important (besides what has been mentioned already under 3, 4 and 5):

6. The molecular volume of the adsorptive,

7. The inner volume of the adsorbent,

8. The compressibility of the adsorptive.

It is obvious that all these magnitudes cannot be expressed in one concise useful equation.

As is evident from this summary only in the very first part of the isotherm are the chemical forces very important.

The adsorption at greater concentrations may be expressed in a physical theory, such as that of Goldmann and Polanyi, but from this it may never be concluded that the adsorption is not specific and has nothing to do with chemical forces.

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SOME RECENT ADVANCES IN THEORETICAL ORGANIC CHEMISTRY[1]

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I. INTRODUCTION

Theoretical organic chemistry appears at the present time to be in a transitional phase of development. It is becoming increasingly difficult to reconcile experimental developments with the classical theories, and as yet relatively few of the host of new theoretical ideas seem to have achieved any considerable success.

The present state of disorder is due chiefly to the influence of modern physics, and may be ascribed for the most part to two general underlying causes. One of these is the attempt to apply the electronic conception of valence to organic compounds. The replacement of the time-honored but meaningless line bond by an electron pair would seem to be certain to revolutionize our ideas of valence and hence most of our fundamental theories. The results in this direction thus far have indeed not been negative, but they have frequently brought confusion rather than clarity.

Most of the classical problems of the science, such as tautomerism, the structure of benzene, rearrangements, relation of physical properties to constitution, steric hindrance—all these and many others—have been translated into the new terms, and each has given rise not, as was to be hoped, to one clear and consistent version, but rather to a number of conflicting speculations. Thus, in going forward, theory has experienced that increased disorder which is characteristic of transitional phases in development.

The second factor contributing to the present state of theoreti-

cal disarray comes from new and improved technical methods
which have given us new types of data on such subjects as crystal
structure, electrical moment, molecular volume and optical prop-
erties. These new data are often very difficult to explain in
terms of our old theories.

In general, it is doubtful whether or not recent theoretical
speculations and improved technical methods have in any very
real sense consolidated the problems before us. Yet in view of
these, it is hard to believe that the classical treatment of the
chemistry of carbon compounds can survive without serious
modification.

This state of affairs greatly enhances the difficulty of preparing
an unbiased report of progress, for it is only here and there that we
can single out a contribution which we can confidently label as a
step forward. It is true, however, that these contributions
present a certain unity in that they are chiefly concerned in some
way with our notions of valence. Accordingly, for this review
there have been selected from the mass of valuable material avail-
able, a few outstanding contributions in the general field of
valence. No attempt has been made to select the material on
the basis of relative merit but, rather, those studies have been
included which, it is felt, best illustrate the general trends dis-
cernible in the development of the field.

For convenience of treatment the development of valence
theory as applied to organic chemistry may be divided, following
the chronological order, into four general phases.

1. The first of these is the concept of valence as made up of a
definite number of discrete linkages—an idea which was first
fully recognized in 1858 when Kekulé showed that carbon is
tetravalent.

2. Next came the question of the spatial arrangement of the
bonds. In 1874 van't Hoff proposed the tetrahedral form for the
carbon atom, thus laying the foundation for modern stereo-
chemistry.

3. As a sort of corollary of this, there arose the question of dis-
tortion of the tetrahedral form—a question which brought for-
ward in 1885 the celebrated strain theory of Baeyer.

4. Finally, following the electron theory put forward simultaneously in 1916 by Lewis and by Kossel, we have the study of the physical nature of the bond.

Although these general problems are no longer new, each continues to stimulate a vast amount of research, and each has brought forth important developments within the period under consideration.[2] It will be convenient, therefore, to discuss the various contributions by reference to their relation to the foregoing outline.

II. CONSTANCY OF VALENCE NUMBER

The constancy of the valence numbers of carbon, hydrogen, oxygen, nitrogen and other elements commonly found in organic compounds long ago reached the stage of certainty which corresponds to that of a law rather than of a theory.   Indeed, the interest in this connection has long since come to be centered rather about the exceptions to this law.   Thus we have the development of the chemistry of divalent and trivalent carbon, of divalent nitrogen and of univalent oxygen in which these elements exhibit unusual valence numbers.   The classification of free radicals as "odd molecules", i. e., molecules having an unpaired electron, has given a satisfactory explanation of their peculiar properties. In general, therefore, the behavior of these compounds has been such as to "prove the rules" of normal valence.

Of unusual interest is the announcement by Paneth and Hofeditz of the production of free methyl by thermal decomposition of lead tetramethyl (1).   Subsequent work by Schultze and Müller (2) has shown, however, that Paneth's observations may be ascribed to the action of atomic hydrogen.   The conclusions of Paneth are thus left open to question.

Among abnormal valence compounds those of divalent carbon have not yet been adequately fitted into our general picture. For this reason the work of Scheibler in this field commands first attention.   Scheibler and Ziegner, in an investigation of the

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[2] An attempt has been made to restrict this review to the developments which have appeared during the period from 1924 to 1929, inclusive; but, as will be seen, the discussion has required frequent reference to earlier papers.

mechanism of the acetoacetic ester condensation (3), discovered a general method for the preparation of ketene acetals—a class of compounds hitherto practically unknown. The method consists in treating an ester with an equimolecular amount of the sodium derivative of the ester in cold dilute ether solution. The addition product when decomposed by water yields the ketene acetal:

$$\begin{bmatrix} \begin{array}{c} R \\ \diagdown \\ \ CH{-}C{=}O \\ \diagup \diagdown \\ R OR \\[4pt] R ONa \\ \diagdown \diagup \\ C{=}C \\ \diagup \diagdown \\ R OR \end{array} \end{bmatrix} \xrightarrow{\;H_2O\;} \begin{array}{c} R \\ \diagdown \\ \ CHCO_2Na \\ \diagup \\ R \end{array} \; + \; \begin{array}{c} R OR \\ \diagdown \diagup \\ C{=}C \\ \diagup \diagdown \\ R OR \end{array}$$
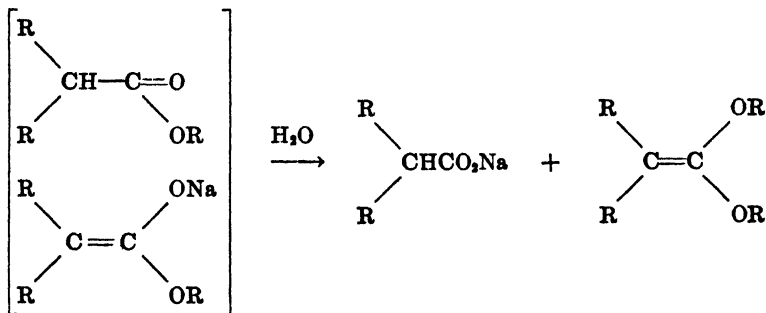
The most interesting of the acetals is that obtained from ethyl diethoxyacetate:

$$\begin{array}{c} C_2H_5O OC_2H_5 \\ \diagdown \diagup \\ C{=}C \\ \diagup \diagdown \\ C_2H_5O OC_2H_5 \\ \text{I} \end{array} \qquad\qquad \begin{array}{c} C_2H_5O \\ \diagdown \\ C \\ \diagup \\ C_2H_5O \\ \text{II} \end{array}$$
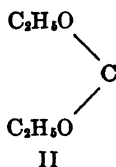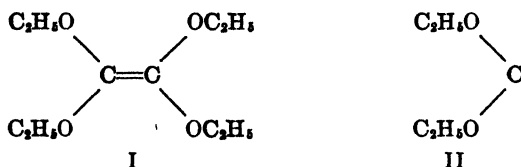
This should lead to tetraethoxyethylene (I). The product obtained, however, has only half the calculated molecular weight and has been assigned the structure II—diethoxymethylene—in which there is a divalent carbon atom.

The physical and chemical properties are in good agreement with this formula. The compound, like ethers and ordinary acetals, is stable to alkali, and is readily hydrolyzed in the presence of acids to give carbon monoxide and alcohol:

$$(C_2H_5O)_2C + H_2O \longrightarrow 2\ C_2H_5OH + CO.$$

When heated the acetal yields carbon monoxide and diethyl ether:

$$(C_2H_5O)_2C \longrightarrow C_2H_5{-}O{-}C_2H_5 + CO.$$

It is not attacked by bromine and only slowly by alkaline permanganate. There is a very marked exaltation of the molecular refractivity. Diethoxymethylene is of particular interest among divalent carbon compounds because it is the first example containing a divalent carbon atom attached to two univalent radicals (4).

Although the existence of diethoxymethylene appears to be consistent with the dissociation series of Staudinger and Engle (5), very recent work has shown that it nevertheless occupies a unique position. Scheibler and Baumann (6) have shown that unsymmetrical diethoxydiphenoxyethylene is stable to heat. It is interesting to note also that tetramethyltetrathioethylene and tetraethyltetrathioethylene have likewise been shown to be stable to heat (7).

III. SPATIAL ARRANGEMENT OF BONDS

The second phase of valence development, which concerns the spatial arrangement of the bonds, has produced an adequate theoretical explanation of the facts of stereochemistry by the assumption of a tetrahedral form for the carbon atom. Much dispute, however, exists over the question of a tetrahedral form for nitrogen. Of first interest in this field, therefore, is the work of Mills and his students with reference to the nitrogen atom in ammonium compounds. These investigators have continued to add to the evidence favoring the tetrahedral as opposed to the pyramidal form for the nitrogen atom in these compounds. In 1925 Mills and Warren (8) resolved 4-phenyl-4'-carbethoxybispiperidinium-1, 1'-spirane bromide.
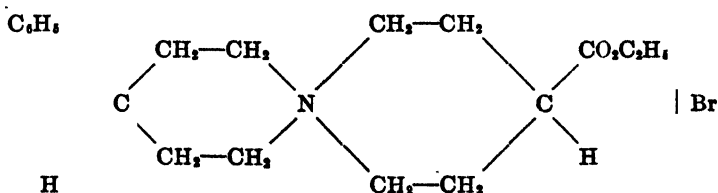
It had previously been shown that:
1. The four bonds of nitrogen are interequivalent.

2. Quarternary ammonium salts containing four dissimilar groups are resolvable into enantiomorphous forms.

3. Position isomerism does not occur in these compounds.

The pyramidal and the tetrahedral forms are, therefore, the only ones which explain the facts.

It is evident that if the nitrogen atom in the spirane bromide has the pyramidal form there will be a plane of symmetry and, therefore, no possibility of resolution into enantiomers. The tetrahedral form, on the other hand, is asymmetrical and should be resolvable. Mills, Parkin and Ward (9) have continued this study by investigating the isomerism of compounds of the type:
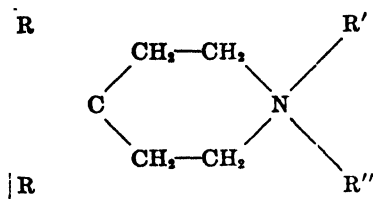
According to the tetrahedral formula these should exist in two geometrical non-resolvable isomers which become identical when R' and R'' are the same. On the other hand, a pyramidal nitrogen atom would give rise to two resolvable compounds in each case; when $R' = R''$ two geometrical isomers would occur. Each of the five different salts used was found to exist in two geometrically isomeric forms, thus proving that in these compounds also the nitrogen atom is tetrahedral rather than pyramidal.

A similar disposition has been made of the case of the dimethyltelluronium dihalides which were reported by Vernon (10) to exist in two stereoisomeric forms. This represents one of the very few instances in which the existence of isomerism in quadrivalent compounds has required the assumption of a planar arrangement of the bonds. In a recent paper, however, Drew (11) has shown that the supposed stereoisomers of Vernon are actually different structurally. A return to the tetrahedral arrangement is thus made possible in the case of the tellurium atom in telluronium compounds.

A decision in favor of the tetrahedral distribution of bonds has

apparently been reached also in the case of the central carbon atom in pentaerythritol for which Mark and Weissenberg (12) had proposed the pyramidal form in order to explain certain crystallographic data.   Resolution studies by Böeseken and Felix (13) and recent x-ray data by Knaggs (14) have thrown the balance of evidence in favor of the commonly accepted tetrahedral configuration.

IV. VALENCE DISTORTION

In connection with the third phase of development—the question of distortion of linkages—we find considerable disagreement and much progress within the past few years.

1. Stereoisomerism of diphenyl compounds

The conception of a valence bond as directional and possessed of a certain degree of rigidity finds support in the isomerism exhibited by certain derivatives of diphenyl.   A large number of these have been found to be resolvable into pairs of mirror images. Christie and Kenner (15) have resolved compounds of types III and IV.   Compounds of type IV have also been resolved by Meisenheimer and Höring (16) and by Kuhn and Albrecht (17). More recently Moyer and Adams (18) have effected the resolution of two compounds of type V.

III   IV   V
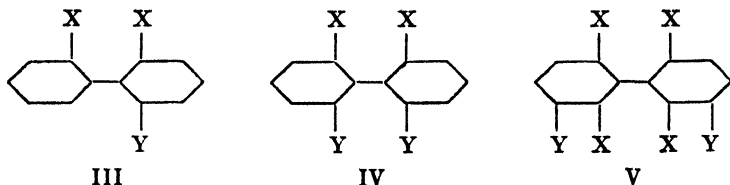
The most acceptable explanation of this type of isomerism is the purely mechanical one of Bell and Kenyon (19) and Mills (20), namely, that the groups in the *ortho* positions act as obstacles to free rotation.   This view is supported by the fact that, in general, these compounds are difficult to racemize.   A further confirmation of the correctness of this view has been furnished by Stanley and Adams (21) who find that when one of the restricting groups

is fluorine, which has a very small atomic volume, racemization takes place rapidly. Thus active difluorodiphenic acid is readily racemized.

2. Strain theory

The idea that valence bonds possess a certain degree of rigidity is likewise involved in the new developments in strain theory.

Large rings. The discovery by Ruzicka (22) and his students that the stable, naturally occurring substances muscone and civetone are constituted of large carbon rings of 15 and 17 members,

Civetone   Muscone
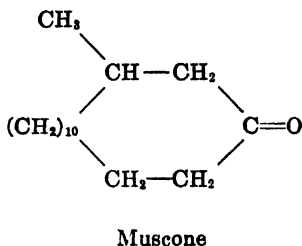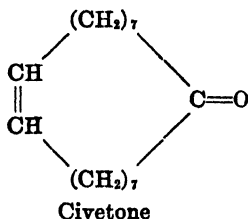
respectively, has at last set aside the Baeyer postulate regarding the instability of large rings. These investigators, following the lead of nature, have already achieved far-reaching synthetic results in the field of large carbon rings.

By the distillation of thorium and yttrium salts of suitable dibasic acids Ruzicka and his co-workers (22) have prepared cyclic ketones constituted of from 9 to 21 members; also those of 29 and 30 members:
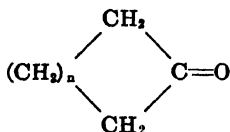
Diketones of the type
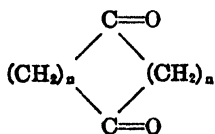
are formed at the same time; of this series those of 16, 18, 20, 22 and 30 members have been isolated and studied. By reduction of the mono- and diketones the corresponding hydrocarbons are obtained, and of these those of 15, 16, 17, 18 and 30 members have been reported.

The outstanding feature of this work, at least from a theoretical point of view, is the fact that all of these compounds appear to be fully as stable as five- and six-membered rings or, for that matter, as their straight-chain analogues. Thus, cycloheptadecanone was passed over thoria at 400–420° and recovered unaltered. Cyclopentadecane and cycloheptadecane were recovered completely after treatment with phosphorus and hydrogen iodide at 250.° In other words, there is no positive evidence that these compounds involve "strain" in the Baeyerian sense. This is, of course, entirely in agreement with the Sachse-Mohr theory of strainless rings (24).

Strainless rings. That carbon rings constituted of more than six carbon atoms exist in strainless multiplanar configurations now seems certain. If one constructs a model of one of these rings, using tetrahedral atoms, he will find that the model will naturally assume a multiplanar unstrained form. That the ring should assume the strained uniplanar form when a strainless form is possible does not seem very likely, and now that we know that the large rings are stable there remains no reason to ascribe to them a structure postulated solely to explain their supposed instability.

This new point of view carries with it certain new possibilities of isomerism and of stable endocyclic bridges, and already much progress has been made along these new lines.

Hückel and his co-workers (25) have discovered a number of new cases of isomerism in bicyclic systems which are predicted by the strainless ring theory, and are exceedingly difficult to account for on the basis of uniplanar rings. One or two examples will suffice to show the general type of compound involved. Decahydronaphthalene has been found to exist in two forms. Hückel represents them as shown in figure 1. Similarly, Hückel (26) has isolated four β-hydroxydecahydronaphthalenes and four β-

aminodecahydronaphthalenes, the number in each case being that predicted by the theory.   Many additional cases of isomerism of this type have since been reported.

Endocyclic bridges.   Another type of evidence in favor of the strainless ring theory is to be found in the existence of numerous types of endocyclic bridge structures which, to judge from their stability, are nearly, if not quite, without strain.   It is not possible to give these compounds even moderately unstrained configurations on the basis of uniplanar rings.   The Sachse-Mohr theory, on the other hand, gives to them multiplanar forms which would seem to be more nearly in accord with the facts.

(cis)   (trans)
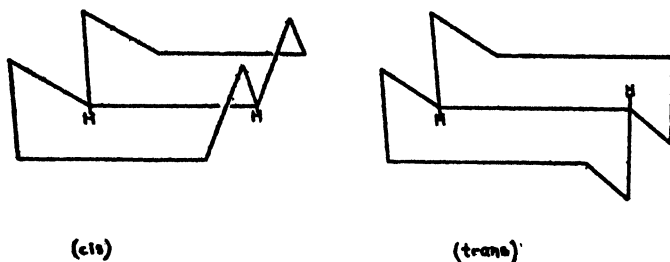
FIG. 1. TWO FORMS OF DECAHYDRONAPHTHALENE

This is admirably illustrated by the important synthetic method of Diels and Alder (27), who have shown that the anhydrides of certain unsaturated acids react with compounds containing a system of conjugated double bonds to give 1, 4 addition products.   Thus, maleic anhydride adds to butadiene as follows:
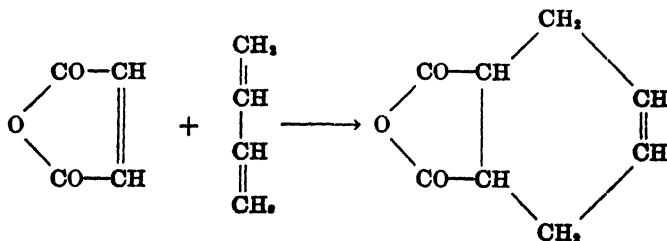
In this same manner maleic anhydride adds to cyclohexadiene:

$$
\begin{array}{cccc}
 & \text{CH} & & \text{CH} \\
\text{CO—CH} & \text{CH} \quad \text{CH}_2 & \text{CO—CH} \quad \text{CH}_2 \text{ CH} \\
\text{O} & & \text{O} \\
\text{CO—CH} & \text{CH} \quad \text{CH}_2 & \text{CO—CH} \quad \text{CH}_2 \text{ CH} \\
 & \text{CH} & & \text{CH}
\end{array}
$$

VI
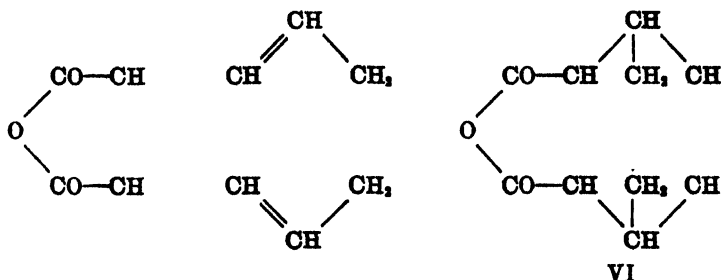
Compound VI is a good example of a large class of compounds the stability of which can be accounted for more satisfactorily on the basis of strainless rings than on the basis of uniplanar rings.

High molecular weight polymers. It should be mentioned that large heterocyclic rings have also been studied. Kerschbaum (28) has shown the essential constituent of vegetable musk to be a lactone of 17 members:

$$
\begin{array}{c}
(CH_2)_r\!\!-\!\!CO \\
CH \\
CH \\
(CH_2)_r\!\!-\!\!CH_2
\end{array}
$$
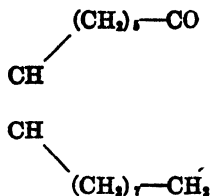
By oxidation of the corresponding cyclic ketones with Caro's acid, Ruzicka and Stoll (29) have prepared lactones of the type

$$
\begin{array}{c}
C\!\!=\!\!O \\
(CH_2)_n \\
\end{array}
$$
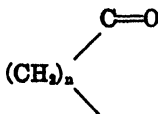
containing rings of 13, 14, 15, 16 and 17 members. Similar compounds have been prepared by Lycan and Adams (30) from ω-hydroxy acids. According to Staudinger, Carothers and others, large rings of this type probably also exist in high molecular weight polymers.

V. THE ELECTRON THEORY OF VALENCE

The chief value of the electron theory of valence has been in the explanation of the differences which exist between bonds. For, although previous to 1916 there was no clear idea as to the physical nature of bonds, the evidence showed that they were not all alike. They were of three distinctly different types and served to divide chemistry into as many apparently irreconcilable groups. How the advent of the electron theory has removed these barriers and given us a consistent picture of the whole will be best appreciated by a glance at the situation which existed in 1916 and the historical developments which led up to it.

At that time there were recognized three types of bonds, each more or less successful in its own domain but of little or no value outside of it. There was the ionizing type of bond, dating from 1812 when Berzelius put forth his celebrated theory of chemical union by electrostatic attraction. Although long in disrepute, the Berzelian theory in modified form still served to explain the properties of a large number of inorganic compounds.

The rise and development of organic chemistry is inseparably linked with the non-ionizing type of bond, which seemed to have nothing in common with the ionizing bond and, beginning about 1840, served to split the science of chemistry into the two major divisions which exist today.

About 1892 Werner put forth his theory of coördination and, in order to account for the properties of the compounds under consideration, invented a third type of valence—the coördinate. By 1911 the body of facts in support of Werner's ideas had shown that this new type of valence was as successful in its own domain as were the older types in theirs.

1. *The polar bond*

The ionizable or polar bond was given an adequate explanation in Kossel's early paper, in which he ascribed the electrostatic bonding force to the passage of an electron from one atom to the other. This gives one of the atoms an extra electron and, therefore, a negative charge. The other atom, having lost one elec-

tron, is positively charged, and what has been called the valence bond is the electrostatic attraction of these two oppositely charged ions.

2. *The non-polar bond*

In Lewis' paper, published in 1916, it is postulated that the non-ionizable or non-polar bond consists of a pair of electrons shared jointly by the two atoms, each contributing one electron to the pair.   The idea that the bonding pair is often shared unequally and in the extreme case is taken over entirely by one of the atoms served to explain the observed differences in polarity.

3. *The semipolar bond*

The coördinate or semipolar linkage of Werner has not been so easy to explain.   It turns out to be a bond consisting of a pair of electrons, both of which are contributed by one and the same atom.   Actually this type of bond may be thought of as a double bond made up of one non-polar bond and one polar bond.   For, since the electron pair is furnished solely by one of the uniting atoms, this atom effectually loses one electron (one half of the pair) and the other atom gains it.   The donor, therefore, carries a positive charge and the acceptor a negative charge.   The case of the amine oxides is a good example.

$$\text{R} \atop \overset{..}{\underset{..}{\text{R:N:O:}}} \atop \text{R}$$
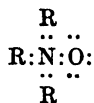
Here the oxygen atom in sharing the lone pair of the nitrogen atom has seven electrons and is therefore negatively charged. The nitrogen atom having given up half of its lone pair of electrons is positively charged.

It is evidence in support of this explanation of coördination with which we have had to do in organic chemistry during the past few years.   This work has indicated that (*1*) *there are two distinct types of double bonds* and (*2*) *one of these types is unsymmetrical.*

4. *The parachor*

The division of double bonds into non-polar and semipolar groups has been accomplished through Sugden's concept, the parachor (31). This quantity, which is a measure of molecular volume, is arrived at from Macleod's equation for the relationship between surface tension and density for normal liquids,

$$\gamma = C (D - d)^4$$

where γ = surface tension, D = density of the liquid and d = density of the vapor, all measured at the same temperature. For non-associated substances, C is a characteristic constant independent of temperature.

If the fourth root of C is multiplied by the molecular weight we get

$$C^{\frac{1}{4}} M = P = \frac{M}{D - d} \gamma^{\frac{1}{4}}$$

where P has the dimensions of volume and, for low temperatures where d is small, is in fact the molecular volume.

This quantity P, known as the parachor, has been found to be related to chemical composition and is an additive function of the atomic and structural units. The presence of a double bond, for example, has been found to increase the parachor by 23.2 units. This value holds for all double bonds involving carbon but in many cases of double bonds between other elements, such as sulfur and oxygen or nitrogen and sulfur, an entirely different value of -1.6 units is obtained. The remarkable thing about these results is that the values for the double bonds examined fall sharply into one or the other of these two classes. These results indicate that double bonds are of two classes.

The final proof that the double bonds of parachor values of -1.6 correspond to the semipolar linkages came from certain studies which have shown these bonds to be unsymmetrical. In the sulfur compounds, for example, sulfoxides and sulfonic esters of the types VII (32) and VIII (33) should possess semipolar

bonds. The plausibility of this assumption will be more apparent if we write the electronic structures for the compounds:

$$CH_3C_6H_4 \diagdown \; S^+ \!\!-\!\! O^- \; \diagup \; C_2H_5O$$
VII

$$CH_3C_6H_4 \diagdown \; S^+ \!\!-\!\! O^- \; \diagup \; H_2NC_6H_4$$
VIII

$$CH_3C_6H_4 : \overset{..}{\underset{..}{S}} : \overset{..}{\underset{..}{O}} :$$
$$OC_2H_5$$

$$CH_3C_6H_4 : \overset{..}{\underset{..}{S}} : \overset{..}{\underset{..}{O}} :$$
$$H_2NC_6H_4$$
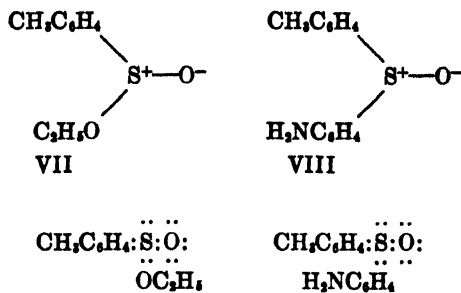
These predictions have been verified by Phillips and his students, who have been able to resolve these compounds into pairs of mirror images. The presence of the semipolar bond is thus proved, for otherwise the molecule would be symmetrical and unresolvable.

These authors have subsequently resolved the sulfilimine (34)

$$CH_3C_6H_4SO_2 : \overset{..}{N} : \overset{..}{\underset{..}{S}} : C_6H_4CO_2H$$
$$CH_3$$
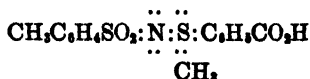
in which the asymmetry is referred to a semipolar bond between a sulfur atom and a nitrogen atom. Bell and Bennett (35) have extended the work in this field by a study of the disulfoxides. 1,4-Dithiandisulfoxide has been shown to exist in two geometrically isomeric forms:

$$\begin{array}{ccc} & CH_2CH_2 & \\ \diagup & & \diagdown \\ ^+S & & S^+ \\ | \diagdown & & \diagup | \\ ^-O & CH_2CH_2 & O^- \end{array}$$

$$\begin{array}{ccc} & CH_2CH_2 & O^- \\ \diagup & & | \\ ^+S & & S^+ \\ | & & \diagup \\ ^-O & CH_2CH_2 & \end{array}$$
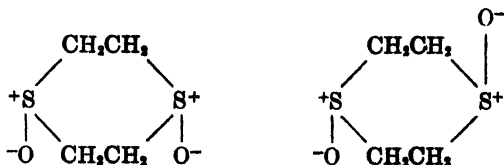
During the present year these authors have examined the dioxides and trioxides of trimethylene trisulfide (36). According to theory there should be two dioxides and two trioxides. Experiment has fully confirmed these predictions. Bell and Bennett have not

only isolated two dioxides and two trioxides but have succeeded in determining the configuration in each case.

IX

XI

X

XII
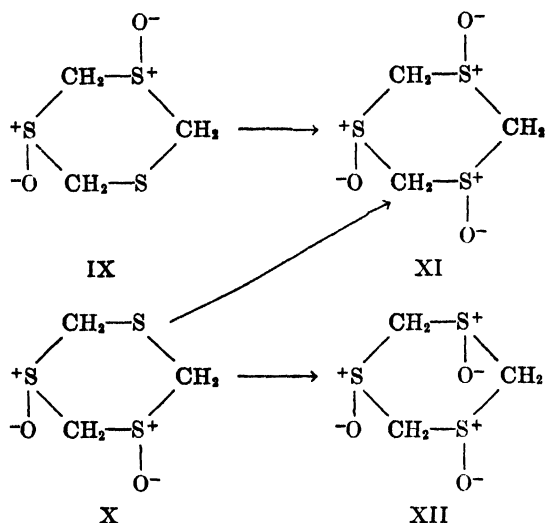
The structure of XI follows from the fact that it is obtained from both IX and X. XII can be obtained only from X. This establishes at once the structure of IX and X as well as that of XII.

5. *Optically active aci-β-nitrobutane*

A further contribution as to the nature of the semipolar bond has been made by Kuhn and Albrecht (37), who have isolated the sodium salt of active β-nitrobutane and have found that it is optically active. They represent the nitro compound and its active salt by the following formulas:
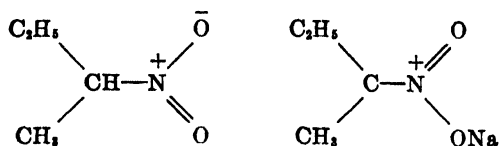
Thus, according to Kuhn and Albrecht, the reaction involves the intramolecular displacement of a semipolar double bond. It is

noteworthy that this is the only instance in which a semipolar character has been suggested for a double bond involving a carbon atom.

6. *Chelate derivatives of diketones*

It has long been known that many metal enolates of β-diketones exhibit anomalous physical properties in that they are not salt-like, but are very soluble in organic solvents and can be distilled or sublimed. Following the suggestion of Werner, these have generally been regarded as internal coördination compounds.

The nature of these derivatives is well illustrated by the trimethyl platinum acetylacetone (XIII) of Menzies (38), the dimethyl thallium acetylacetone (XIV) of Menzies, Sidgwick, Cutcliffe and Fox (39)

XIII   XIV
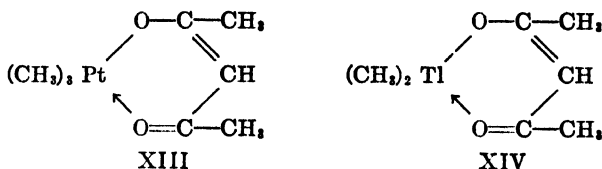
and the beryllium benzoyl camphor of Burgess and Lowry (XV) (40).

XV
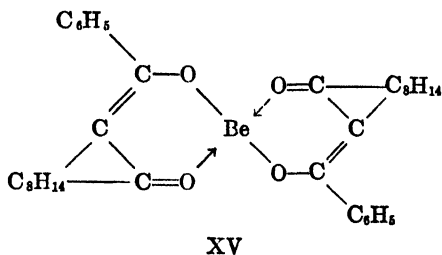
In terms of the new valence theory the beryllium atom in XV is supposed to complete its octet by coördination with the two carbonyl oxygen atoms. Thus it is linked to two of the oxygen atoms by non-polar bonds and to the two remaining oxygens by semipolar bonds.

The nature of the valency of the metals in this type of com-

pound has been put on a firm experimental basis by Mills and Gotts, who have studied the beryllium derivative of benzoylpyruvic acid. According to the theory, this compound should have the following structure:
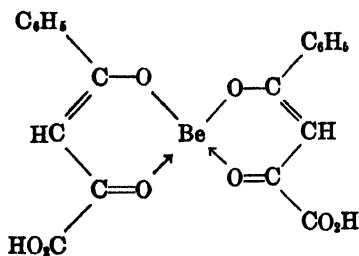
It should be mentioned also that this formula is supported by the x-ray findings of Morgan and Bragg (41), who state that in this compound the beryllium atom is surrounded by four oxygen atoms in a tetrahedral arrangement.

This idea of a tetrahedral arrangement furnishes at once a tool whereby the correctness of the structure may be tested, for in that case the molecule as a whole will be asymmetrical and, therefore, capable of resolution into enantiomorphous forms. Experiment has fully supported these ideas. Mills and Gotts (42) prepared the active forms of the dimethylammonium salt of beryllio phenylpyruvic acid.

The resolution of this compound demonstrates at once that the beryllium is actually bound simultaneously to the four oxygen atoms and that these are arranged in the tetrahedral form. It is noteworthy that the active forms of the compound are racemized with the utmost ease—a result which is in entire agreement with the formula. Similar results were obtained with the zinc and copper derivatives of phenylpyruvic acid.

From these results emerges the conclusion that the bonds involved in coördination compounds have the directional properties of ordinary non-polar bonds—are, in a word, like the semipolar bonds which are found in such compounds as amine oxides and sulfoxides.

7. *Divalent hydrogen*

In view of the information now available with reference to coördination compounds in general, it seems probable that the driving force behind coördination reactions is the tendency of atoms to complete stable shells. In most instances the stable group is the octet, but in a few compounds the stable shell would appear to contain ten, twelve or even more electrons. It has been suggested by Huggins and by Latimer and Rodebush that hydrogen may become divalent by coördination in such a way as to complete a shell of four electrons. This theory, which has achieved signal success in inorganic chemistry, has been used by the organic chemist in explaining molecular association.

It is probable that the molecular association of water, hydrogen fluoride, alcohols and other hydroxyl-containing compounds is due to coördination through hydrogen:

$$
\begin{array}{cc}
\text{H} \quad \text{H} & \\
\text{H:O:H:O:} & \text{H:F:H:F:}
\end{array}
$$

Evidence of a conclusive nature in favor of this has been brought forward by Sidgwick and his students in an investigation extending over the past fifteen years.

It has been shown, for example (43), that in β-diketones the enol form is less polar, i.e., more volatile, more soluble in organic solvents and less associated than the keto form. It cannot, therefore, have a hydroxyl group, but could exist in a chelated form (XVI) which would be expected to show the observed non-polar properties.

XVI   XVII
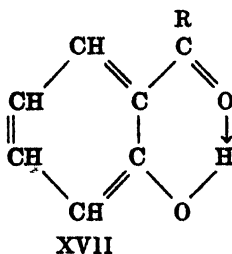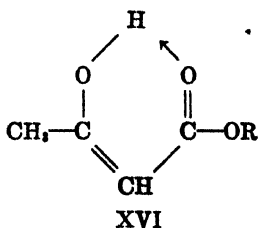
In a similar way certain *ortho*-substituted phenols (44) have been shown to be less associated, more volatile and in general less polar than their *meta* and *para* isomers. The assumption that these compounds are chelated through hydrogen (XVII) again gives a satisfactory explanation of their anomalous properties. For the anomalously non-polar character appears only when the substituent next to the hydroxyl group is NO_2, CHO, or CO_2H, i.e., a group which has a lone electron pair to conjugate with the hydrogen, and is absent when the substituent is an alkyl group, a group which can furnish no lone electron pair.

VI. CONCLUSION

In conclusion, it might be well to point out certain general trends which are apparent in the development of valence theory at the present time.

1. The so-called classical considerations, *viz.* the number of bonds, their spatial arrangement and the problem of bond distortion, still engage the attention of the majority of investigators. These problems continue to yield highly significant results, illustrative examples of which have been mentioned.

2. Certain rather surprising developments, notably the explanation of the isomerism of diphenyl compounds and the theory of strainless rings, seem to require the return to a more rigid type of model for the tetrahedral carbon atom.

3. The electron theory of valence has consolidated the various fields of chemistry by an explanation of the differences in the bonds characteristic of these fields.

4. Finally, it might be pointed out that the great importance of the problem of reaction mechanism has gained more general recognition. Nothing is more eloquent of this than the vast amount of work which has been done in an attempt to apply the new valence theory to the problem. Moreover, nothing shows more clearly than these attempts the real inadequacy of the theory in its present form. Reaction mechanism certainly calls for a dynamic theory of valence, and in this respect the new theory is open to essentially the same criticism as was the old—it is a static theory. It might be predicted, and it is certainly to be

hoped that the next great step ahead in the field of valence will
be in this direction.

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MICELLES AND BASE EXCHANGE[1]

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The term "micelle" was invented by Nägeli (1) to represent a colloidal particle. The term has been used in a number of senses, many of them loosely defined. We shall attempt in this paper to amplify the discussion of the thermodynamic consequences of the term in its broadest aspect, and we shall particularly study the electrolytic micelle as used by McBain (2), which postulates that a simple ion formed by the dissociation of certain electrolytes may be considered replaced by a heavily hydrated polyvalent ion or micelle. The thermodynamic and physical properties of soap solutions and of alkali silicate solutions have been explained by means of this concept (3). We shall also consider the extension of the idea of micelles to complexes and the property of base exchange in relation to electrolytic micelles, with particular reference to a rigid micelle ion or group of rigid micelle ions.

The class of substances which might be called by the term "micelle" stands intermediate between a substance of the simplest molecular constitution as, for instance, dilute helium gas and one of the most complex. Practically, we may well limit ourselves to a consideration of substances more complex than simple molecules or ions or ionic radicles, as H_2O, Na^+, SO_4^{--}, etc. We might presume that the term "micelle" included all more or less definite complexes, but before discussing the thermodynamics of such systems, we shall consider the chemical individuals of which they are composed. We might divide the possible complexes on the basis of the type and degree of chemical binding which marks the

various kinds of complexes or micelles. Without going too far into the mechanism of these chemical bindings we may roughly divide them into two main groups,[2] called "electronic bindings" and "interionic forces."

It is not possible to draw a definite line of demarcation between the two groups, and some may wish to offer a single mechanism to explain the two groups. For the purpose of our discussion, it is unnecessary to define the type of binding. As we shall see, certain types of complexes are more simply considered, if the assumption of the predominance of a particular type of binding is made. Thus, the assumption of electronic binding in a crystal of diamond, or in a stable complex such as $Ag(NH_3)_2{}^+$ or $Ag(CN)_2{}^-$, enables us to predict that a crystal of diamond will act as a single molecule, or that the law of definite proportions will account for the constancy of the composition of the complex. On the other hand, the assumption of pure interionic forces in such crystals as those of potassium chloride explains the crystal lattice and the ease with which ions are formed from these crystals in a saturated water solution. In like manner, the assumption of forces closely related to interionic forces, as the explanation of the grouping of water molecules around potassium and chloride ions in solution, offers a mechanism for observed phenomena. We shall also recognize as electronic bindings such polymeric combinations as are frequently met with in organic chemistry, as the polymerization of formaldehyde, or cyanogen, and which may be the explanation of the ready "adding on" of silica to $HSiO_3{}^-$, or of CrO_3 to $CrO_4{}^{--}$.

The conception of micelles, from a thermodynamic standpoint, is essentially that a system composed of micelles and solvent forms a homogeneous phase—homogeneous in the sense that the composition and properties of any particular portion of the phase is the same as that of any other portion, providing we take the portion so large that its average composition is the same as the average composition of every other portion, and that statistical

<hr />

[2] A third group may include the combination of such molecules as carbon tetrachloride, forming a liquid or solid in which the molecules are held by some force which is not here named.

methods are valid. Thus, if we consider a solution of sugar *microscopically* and portions of the phase so minute that the number of sugar molecules is so small that statistical methods no longer obtain, or if we consider a portion of the homogeneous phase of dimensions of the order of magnitude of the molecules composing that phase, one may no longer consider it homogeneous. So, when we speak of micelles in rapid equilibrium with their simple products of dissociation, we are thinking of a portion of a homogeneous phase sufficiently large that molecular discontinuities are not recognized. When we think of the micelle in the limit, that is when all the material in a solution aggregates into a single micelle, we have reached a point where it is difficult to choose so large a quantity of solution that the individual portions may all be said to have the same composition and properties. However, we may still apply statistical methods in just the same way that we apply such methods to the vapor pressure of tungsten at ordinary temperatures, where the concentration of tungsten atoms in equilibrium with tungsten metal is less than one in the whole sidereal universe.

THE TYPICAL CRYSTAL AS A MICELLE

Just as it is valuable to consider such an apparent absurdity as the concentration of tungsten vapor in equilibrium with the metal at ordinary temperatures, let us carry the idea of micelle formation to an almost absurd limit and from this viewpoint consider the mixture of a single crystal or of a small number of crystals with the saturated solution.

Let us study not a solution which is in equilibrium with a single potassium chloride crystal but rather one in equilibrium with small crystals which do not differ appreciably in thermodynamic properties from a single one. Thus we may consider (4) the reaction

$$K^+ + Cl^- = 1/n(K_n^{n+} + Cl_n^{n-}); \Delta F^\circ = 0; K = 1 \qquad (1)$$
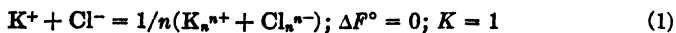
where n is the number of potassium or chloride atoms forming the crystal particle with which the solution is in equilibrium, and n^+ and n^- are the number of charges associated with each micelle.

If we follow the usual custom in dealing with micelles, we will refer their activity to the same standard state as that used for the ions, namely the hypothetical molal solution of potassium and chloride ions.   Consequently we write for the above reaction:

$$\Delta F° = 0; \; K = (m' \pm \gamma')^{2/n} (K_n Cl_n)/(m \pm \gamma)^2 (KCl) = 1. \tag{2}$$

The molality of the micelle is the number of moles of potassium chloride crystals per thousand grams of water, which is equal to the number of crystals per thousand grams of water (or 55.51 moles) divided by Avogadro's constant (6.06×10^{23}), and will consequently be a very small number.   By virtue of the principles which we have already given in another place (3f), we should expect the activity coefficient of such a solution of micelles to be very small because of the large number of charges associated with each ion of the crystal micelle.   However, it will be noted that the product of the molality and activity coefficient of the crystal micelle is raised to the $2/n$th power which is a very small power, and consequently the value of the activity of the crystal micelle in equilibrium with potassium and chloride ions is the same as that of a potassium chloride solution as ordinarily defined.   It is obvious, then, that, so far as our thermodynamic treatment is concerned, the micelle crystals obviate the necessity of considering a distinction between a homogeneous and a heterogeneous solution, for we may make n as large as we please.

However, in ordinary practice, we have found it more convenient to take the activity of the solid in the large crystal as unity and therefore to write the equation:

$$KCl(s) = K^+ + Cl^-; \; \Delta F° = -RT \ln (m\gamma)^2(KCl) \tag{3}$$

whence, combining equations 1 and 2, we find

$$KCl \, (s) = 1/n(K_n^{n+} + Cl_n^{n-}); \; \Delta F° = -RT \ln (m\gamma)^{2/n}(K_n Cl_n). \tag{4}$$

If in the above treatment we had taken the size of the crystal such that $2n$ rather than n potassium ions and $2n$ chloride ions were united to form the micelle, then the molality of the crystal micelle per gram-mole of KCl would have been one-half that which we have used.   With large crystals the molal free energy is practically independent of the size of the crystal, hence since

$(m \pm \gamma)^{3/n} = (m' \pm \gamma')^{1/n}$ where $m' = 0.5m$, the activity coefficient must change in such a way as to satisfy, no matter what the size of the crystal, so long as it is so large that the molal free energy remains constant.

It is immaterial for the thermodynamic argument whether or not the various potassium and chloride ions in the crystal micelle neutralize the electrical effect of the one upon the other, as this is taken care of in the measured activity coefficient. It is our purpose in introducing this more or less fanciful idea to show the import of the conception of micelles in solution, to show the intermediate character of the micelle and to show that, from a thermodynamic standpoint, we are not greatly concerned with the mechanism of surface phenomena. The position of the micelle as an intermediary between the individual molecule of a solution and a crystal has been recognized since the inception of the postulate; but in many cases the idea of the colloid as a distinct phase has been emphasized, whereas we have shown that the conception is that of the crystal or micelle and its saturated solution, which can be treated by the same methods as those used for the homogeneous system.

The reader has no doubt objected that neither potassium nor chloride ions form micelles. We might rather suggest that there are no intermediate steps between the typical ionic solution and the potassium chloride crystal micelles we have studied. Indeed the idea of a micelle (and consequently a homogeneous phase) in the present case has little in its favor, and the formulation on the basis of a heterogeneous system is much more convenient.

<center>MICELLE IONS</center>

The concept of micelles is particularly adaptable when only one of the ion constituents has a tendency to form these aggregates and the other constituent remains in the ordinary ionic form, as, for example, in the case of the soaps and silicates.

We will now consider the case represented by

$$B^- = 1/n \; B_n{}^{n-}; \quad K = (m\gamma)^{1/n}(B_n{}^{n-})/(m\gamma) \, (B^-) \qquad (5)$$

in which the positive ion A^+ does not form intermediate micelles of the type represented for the negative ion in equation 5.

If n has a small value, such as ten, and one-tenth of the stoichiometrical molality of the negative ion constituent is in the form of the micelle, then the molality of the univalent ion is ninety times that of the micelle.   If n is one thousand, and ten percent is in the form of a micelle, then the molality of the univalent ion would be nine thousand times that of the micelle.   And if, in the case of a single crystal of AB, in equilibrium with its saturated solution, we assume that one-tenth of the B ions are present in the AB crystal, then the molality of the B ion constituent in the solution is $9n$ times that of the AB crystal.   But we have seen that the activity coefficient of such a large electrolytic crystal considered as a solute must necessarily be very small, so that the equilibrium constant in equation 5 is essentially zero, and for ordinary purposes such a way of discussing the solution is valueless.   On the other hand, when n is small, we may speak of the molality of the micelle, of its activity coefficient, etc., as such; and it thus represents the first stage in the formation of "insoluble" substances from homogeneous ionic solutions.

When the proper nuclei are introduced into supersaturated solutions of typical crystalline substances, the molecules group themselves in a regular orientation.   So, also, we think of micelles forming larger masses, when, for instance, a 0.2 M potassium palmitate solution at 90°C. is cooled to 0°C. (3c).   The molality of the palmitate micelles of a definite number of charges, which we believe to be arranged in a particular orientation for this molecular species of micelle, is governed by the value of the equilibrium constant of the reaction in which this micelle is formed from its ions, and this equilibrium constant varies with the temperature, depending upon the variation of the partial molal heat contents of the ions and micelles.

Or, we may think of a whole series of reactions of the type:

$$l[B]_n{}^{n-} = [B_m]^{m-} \tag{6}$$

and write equilibrium constants involving the molalities, or molalities times activity coefficients, of the micelles existing as such; and we may say either that we have equilibrium between the two species of micelles or equilibrium between the one species and the ions that have not formed micelles.

We might also postulate the formation of a positive micelle according to the equation

$$A^+ = 1/p \ A_p{}^{p+}; \ K = (m\gamma)^{1/p}(A_p{}^{p+})/m\gamma(A^+). \tag{7}$$

As examples of the positive micelle, we might mention that protein chlorides or sulfates, in their more concentrated solutions, may possibly be considered to be illustrations of positive micelles, although we should wish to examine this point later.

Metathesis of micelle ions

Ordinarily, in speaking of micelle formation, there have been considered only those cases in which the micelle formation is restricted to either the positive or negative ion; and we have not examined specifically cases in which substances are present which would tend to form both positive and negative micelles; although, if our suppositions are correct, we might well expect metathesis to take place, and, at least at the points of contact of the two micellar masses, some of the charge on the positive micelle might be expected to neutralize some of the charge on the negative micelle. But if the micelles were very large, we might also expect to find small positive ions, such as K^+ or Na^+, taking part in the neutralizing of a portion of the charge on the surface of the negative micelles, and small negative ions, such as Cl^-, taking part in the neutralizing of the charge on the positive micelle in such a way as to preserve the electro-neutrality over the whole surface of the resulting substance. This picture is similar to that of the well-known Helmholtz double layer.

As an example, we may mention $Fe(OH)_3$, ferric hydroxide sol (5). We shall assume that it may be considered to be an agglomeration of excess hydrated ferric oxide and hydrated ferric ion arranged in more or less definitely oriented states with Cl^- ions neutralizing the charge. When this sol comes into contact with arsenious sulfide sol, which we might also consider to be a large negative micelle with Na^+ as the neutralizing positive ions, there is formed an "insoluble" substance which retains practically all of such sodium and chloride ions "adsorbed" on the precipitate. It is not likely that the atoms in the respective sols are able to rear-

range themselves in such a way as to form a definite ferric thio-arsenite; it is more likely that they come together and retain to a large extent the individual structures of the micelle ions and thus necessarily give an opportunity for the sodium or chloride ions to compete for the neutralizing of charges in various parts of the clumping surfaces. This merely states that the ferric hydrox-ide sol itself is exchanging places with a certain number of sodium atoms at the surface of the arsenious sulfide sol. We have seen that the larger the number of charges on an electrolytic ion, the smaller the activity coefficient of that ion, and hence these precip-itated clumps will give lower activity coefficients than arsenious sulfide sol of the same size. Indeed, we might picture such a mixture of crystalline clumps with the property of exchange of positive ions at certain points and the property of exchange of negative ions at other points. With large amphoteric protein micelles, e.g. anti-bodies, etc., this is not a particularly new con-ception.

THE TYPICAL IONIC CRYSTAL AS A COMPLEX

Returning to the case of a typical ionic crystal in its saturated or supersaturated solution, we may think of the neutralizing effect of the potassium ion near the six chloride ions in the crystal and of the chloride ion near the six potassium ions in the lattice as enabling the interionic forces to bind the whole into a single particle just as interionic forces or electronic bindings are able to bind their own ions into a micelle in the case of micelle-forming ions. There remains, however, the fact that, when we think of a single crystal, such as a potassium chloride crystal in contact with a solution, we no longer think of it as a colloidal solution; it is more useful to think in other terms. However, as far as the sur-face layer of the crystal is concerned, there are points where the attraction for a positive ion is greater than that for a negative ion, and an equal number of points at which the attraction for a nega-tive ion is greater than that for a positive ion. As a matter of fact, all the atoms in the crystal are ultimately free to take part in a reaction, for if the supply of neutralizing ions in the solution is locally reduced, then another portion of the crystal will dissolve

in order to supply this deficiency. The effect at the surface of a potassium chloride crystal of the points of alternate attraction is to give a certain place orientation to the charges in the solution in the immediate vicinity.

<div align="center">COMPLEXES</div>

We do not wish to enter into a mathematical discussion of the application of an interionic attraction model in this place. But, considered in a qualitative way, the effect of the distributed neutralization of the negative charge, postulated for the chloride micelle in equation 1, by the postulated charge upon the positive potassium micelle is to lower the calculated activity coefficient, just as the "association" assumed by Bjerrum (6) lowers the calculated activity coefficient of potassium nitrate.

Complex ions of the type $Ag(NH_3)_2{}^+$ or $Ag(CN)_2{}^-$ are universally accepted as orthodox chemical entities. These ions take part in equilibria such as

$$AgCl(s) + 2\,HCN(aq) = Ag(CN)_2{}^- + Cl^- + 2\,H^+ \qquad (8)$$
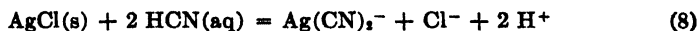
and show in many respects the same kind of behavior as has been attributed to the typical micelles. Thus, the palmitate micelle dissociates when the concentration of the simple palmitate ion in the solution is decreased; and, with these complex ions, the ion dissociates when one of the products of its dissociation is used up.

We think of the formation of the complex of this type as due primarily to electronic binding between the component atoms; but some will prefer to explain the mechanism of their formation upon the basis of entirely interionic attraction relationships.

The complexes we have mentioned have very small dissociation constants, and just as we have acids and bases with small and large dissociation constants, we also have complexes with large dissociation constants. Thus, the divalent and trivalent metal chlorides and sulfates, which in the crystal form, have a great tendency to form double salts, probably form these easily dissociated complex ions[3] of the types $CdI_3{}^-$, $Mg(SO_4)_2{}^{--}$, $Al(SO_4)_2{}^-$, $CuBr_3{}^-$, or $CoCl_4{}^{--}$.

[3] McBain and Van Rysselberge, in an address before a meeting of the California Section of the American Chemical Society at San Francisco, May 11, 1928, re-

These easily dissociated complexes seem to be of interionic type related more closely perhaps to the crystal micelle of potassium chloride which we have chosen as an ultimate limit than to the complexes of the type of $Ag(CN)_2^-$. There is good reason to think that ions more complex than the types we mentioned may be present in very concentrated solutions, for example, of silver chloride in very concentrated hydrochloric acid. If three chloride or iodide ions should unite to form a micelle, the field or charge on the ion would be so great that there might be attracted into this combination certain types of positive ions. Alkali ions are not strongly attracted to the complex, although in very concentrated solutions of potassium chloride we might expect to find evidence for the inclusion of rubidium or caesium ion (9). The difference may well be one of degree for the transference number of cadmium iodide (10) in aqueous solution is explained by McBain by the formation of the complex CdI_3^-, and in concentrated solutions of this salt in propyl and amyl alcohols McBain found evidence for the existence of micelles which would not pass through a membrane which was permeable to the ions as they exist in water solution (7).

With small bivalent and trivalent anions the tendency to form complex ions is much greater. We are familiar with the strong tendency of ferrous, cupric, cadmium, zinc, aluminum, chromium, ferric, etc., sulfates to form double salts with the sulfates of the alkali metals; and the experiments of McBain and Van Rysselberge (7) support the view that these metals enter a complex negative ion leaving the univalent cations to neutralize this charge in the same way that the potassium ion in a strong solution of potassium palmitate provides the means for electro-neutrality in these solutions. Of course, in mixed solutions of divalent or trivalent bases the positive ion which enters the complex depends upon

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ported transference data which showed that the magnesium ion in mixed potassium and magnesium sulfates, the cadmium ion in mixed potassium and cadmium sulfates and mixed magnesium and cadmium sulfates, and the lithium ion in mixed potassium and lithium sulfates, moved to the anode in approximately molal solutions. The phenomena were ascribed by the speakers to the formation of complex anions of the type $Cd(SO_4)_2^{--}$. J. Am. Chem. Soc. 50, 3009 (1928).

the relative complex-forming tendency of these ions with the particular anion.

We may also mention the explanation of the transference numbers of the alkali and alkaline earth casein salts (11). These substances in all probability form micelles in much the same way that the soap micelles are formed. The alkali is found to travel in both directions, and complicated chemical formulas were devised (12) to account for the effect; but if we merely postulate the partial neutralization of the charge on the micelle, by charges of the opposite kind, held in the orientation more strongly than others (complexes) and therefore dragged along with the micelle under the influence of the current, we have an explanation which will fit the facts, and it is essentially the same explanation which is given to explain the transference numbers of cadmium iodide or of cadmium sulfate in potassium sulfate solution.

McBain and Bowden (13) showed that a fraction of the potassium ion in the more concentrated solutions of potassium laurate was carried to the anode, which can be explained by assuming that some of the potassium ions function to reduce the charge on the negative micelle, and in this sense we would say that some complex ion had been formed. Such distributed neutralization of the charge is, however, probably of only secondary importance in this case.

The transference measurements made by Harman (14) with sodium silicate solutions do not definitely show this phenomenon of the partial neutralization of the charge on the micelles. These, however, are to be regarded as smaller aggregates than those of the soaps in the solutions which are considered.

The transference data of Wintgen (15), of Wintgen and Biltz (16) and of Wintgen and Löwenthal (17), for colloidal stannic oxide peptized by potassium hydroxide, for ferric oxide peptized by hydrochloric acid, and for chromic oxide peptized by ammonium chloride, respectively, show that a fraction of the potassium in the first case, and of the chloride in the second and third cases moves with the colloid; in other words, partially neutralizes the charge on the micelle.

We may imagine the structure of these complex ions or micelles

to be somewhat similar to that of the potassium chloride crystal in which the various atoms are held in more or less definite positions, but in which every atom is eventually free to move as it pleases.   The crystal structure of the alums has been definitely determined by Wyckoff (18).   These show the same kind of definite orientation as is shown by the potassium chloride crystal. Our point of departure is that at the surface of the alum crystal, in contact with its saturated solution, potassium ions and some of the complex $Al(SO_4)_2^-$ groups come off, but these complex groups are free to enter into the general equilibria of the solution. Even aluminum ions or sulfate ions themselves may be assumed to dissolve from the surface of the crystal as such.   The preliminary measurements by Latimer and Greensfelder (19) of freezing point lowering of caesium and rubidium alums and an unpublished summary of freezing point measurements, show an abnormally low activity coefficient of the alums.   It is obvious that the binding of the positive ion into the micelle or complex is a differential matter.

ORIENTATION IN MICELLES

McBain (2) has postulated that a micelle formed by, say ten, palmitate ions has a definite orientation which is thought to be that of a flat disk.   This orientation is perhaps a consequence of the electronic bindings.   As a palmitate solution is concentrated, the tendency for micelles with a larger number of ions to form becomes greater, and these are formed not only from the simple ions but also by an agglomeration of smaller micelles. The electronic bindings again must be a predominant characteristic of this union.   The definiteness of the orientation will not be so marked in the case of these larger micelles formed from two or more smaller micelles and will not be as "perfect" as in the case of those formed directly from simple ions.

Let us again consider the formation of a micelle in its simplest terms, i.e., the union of two hydrated $HSiO_3^-$ ions to form a hydrated $(HSiO_3)_2^{--}$ ion.   As we have seen, this implies a certain degree of orientation which is not present in the solution containing only $HSiO_3^-$ ions.   And as more and more of the $HSiO_3^-$

ions combine into the micelle, the number of atoms definitely oriented becomes very great; and the sodium ions associated with them, because of the necessity of maintaining an average electrical neutrality in the solution, are also more or less fixed in their orientation. On the other hand, when a potassium chloride crystal forms from a solution, we have again a difference in the orientation of the ions, and there is a sudden change with very strong and definite orientation forces which may or may not involve, as in the case of micellar formation, the elimination of ionic solvation.

In the case of the acid sodium silicates, we saw (3f) that there was a tendency for the negative ion to "add" silica in varying proportions, and that there was a gradual transition of properties from the sodium silicate of $1 Na_2O : 1 SiO_2$ over to silicates with ratios of as high silica content as $1 Na_2O : 5 SiO_2$. We especially noticed the increasing tendency on the part of the solutions containing large amounts of silica to form micelles. With increasing amounts of silica, the viscosity of the silicates in water became great.

As we consider more and more concentrated solutions, we find the properties merging with those of the glasses, which are ill-defined crystalline substances, the lack of definition of which may, perhaps, be due to the fact that the aggregation of several micelles to form a larger micelle possesses within itself a less definite orientation than the individual micelles that come together. But if sufficient time were given and the thermal conditions were right, these would doubtless form crystals, because we know that glasses become definitely crystalline after a lapse of time.

It is obvious that the forces pertaining to the formation of micelles will not necessarily seek out molecules or micelles of their own kind; hence we may expect to have slipped into the aggregate a molecule or so of the wrong kind, which may account for the indefiniteness of composition of many colloidal substances.

We note that the tendency to form micelles is strongest with those substances that do not form well-defined crystals. The orientation force, in the case of the substances forming well-defined crystals, is sufficient to form immediately the definite crys-

tal lattice. Perhaps the relation between the micelle and the crystal is somewhat analogous to that between the liquid crystal and the crystal. It is perhaps significant that the substances which easily form micelles do not readily form crystals.

There are those who will object to the designation of so simple an oriented aggregation as $(HSiO_3^-)_2$ as a micelle, because of the belief that the more obvious relation is perhaps that of the complex ion. But we have taken such cases as the first step in the formation of the micelle, just as we have taken the crystal or the "amorphous" particle as the limit of the largest possible micelle.

We have treated solutions of visible micelles as a system consisting of a homogeneous phase. We might equally well, in a very real sense, have said that the treatment of the discontinuities, for example as in the Debye and Hückel (20) interionic attraction theory, lead us to consider the system heterogeneous and indeed, when the individual particles, or ions, become of ultramicroscopic size, the usual custom has been to treat these systems as heterogeneous. Either viewpoint will, of course, given an equally correct thermodynamic interpretation of the system, and we are free to use the one or the other, as long as we are consistent. Expediency dictates the system which we will use in any particular case.

BASE EXCHANGE IN GENERAL

All substances that form negative micelles in solution should then possess the differential base exchange properties and *vice versa*. Such systems ought to be realizable in several ways. A lump of gelatin placed in a mixture of chlorides should swell, and the ratio of bases in the gel should be different from that in the body of the solution. If a concentrated sodium soap solution is placed on the inside of a collodion cell and the cell placed in a solution of ammonium chloride, the ratio of the bases should be different.

Some of the ideas here presented may be further illustrated by experiments which, although as far as we are aware have never been performed, must, if our ideas are correct, give the results which we have indicated. If potassium silicate solution, con-

tained within a membrane cell permeable to potassium ion but not to silicate ion, is placed in a beaker containing a sodium chloride solution, then there will be a distribution by which some potassium ion will pass out through the membrane and enough chloride ion will pass in through the membrane to establish the Donnan equilibrium (21), and sodium ion equivalent to the potassium ion which has come out and also to the chloride ion which has gone in, will pass through the membrane.

If we assume that the activity coefficients of the sodium and potassium ions outside the membrane are equal, then the ratio of the sodium to the potassium inside the membrane need not be exactly proportional to the concentrations of these ions outside of the membrane because of the greater specific affinity for one of the ions, due either to a difference in the affinity, or to a difference in the activity coefficient due to the different "sizes" of the ions and a consequent different association in the Bjerrum (6) sense.

If we consider the swelling of gelatin in a mixed chloride solution, the ratio of the two ions inside the gelatin block need not be the same as that outside the block; and if the concentration of one of the substances in the mixed electrolyte is changed, we should expect a change in the concentration of that ion within the block, i.e., we should expect base exchange.

Petrie (22) found that the amount of absorption of certain positive ions, as NH_4^+, K^+, and Ca^{++}, by carrot disks was not equivalent to the amount of absorption of negative ions such as NO_3^-, Cl^-, SO_4^{--}, and explained the phenomena by assuming that chemical exchange of bases, rather than absorption, occurred. Stiles (23) showed that in the absorption of sodium chloride by carrot tissue the excess Na^+ absorbed was replaced by Ca^{++}, K^+ and Mg^{++} in the solution; and similar replacements were found by Redfern (24) and by Stoklasa (25) and his collaborators. There are abundant micelle-forming colloids in the carrot tissue.

Or, consider the case of sodium and calcium soaps in the presence of sodium and calcium ions. Here there are two ways of looking at the question; first, that the calcium ion and soap ion form an insoluble compound, calcium soap. But we might al-

most equally well have said that the tendency of the ions of the soap to form micelles has been increased by the specific attraction of the calcium ions which crowd out the sodium ions in the vicinity of the micelle, and that these micelles then further agglomerate to form the calcium soap which is insoluble. Herein arises the real difficulty in reconciling the viewpoint of the formation of a micelle with that of a so-called insoluble compound, for the question arises as to when a substance is merely insoluble and when we have merely a large single electrolytic crystal, such as that of potassium chloride, in contact with a saturated solution. These two viewpoints must lead to the same thermodynamic result; for, as has been pointed out, thermodynamics does not enquire into the mechanism of a process.

Another case of reversible base exchange is of the type studied by G. McP. Smith (26) and his co-workers, who studied the equilibrium between mixed alkali and alkaline earth metal amalgams and solutions of the chlorides or other negative ions of the same metals. In this case rapid equilibrium is obtained between the two liquid phases, and the relative proportion of a given metal in the amalgam depends upon the ratio of the molalities of that metal in the aqueous phase and upon the relative activity coefficients of the metals or metallic ions in the amalgam and solution, respectively.

In the same way the composition of a mixed crystal of caesium and potassium alum obtained from a slightly supersaturated solution of the salts depends upon the ratio of the molalities of the caesium and potassium ions, and the ratio of the activity coefficients of these ions in the aqueous solution and their activities in the mixed crystal. Also, if a crystal of potassium alum is dropped into a saturated solution of a definite mixed crystal, there will be a dissolution or replacement of some of the potassium ion by caesium ion, but this action will not proceed many layers of molecules into the surface of the crystal because the rate of diffusion into such a dense crystal, with strong orienting forces, is low. We are thus able to grow crystals with alternating layers of different isomorphous salts by transferring from one solution to another.

BASE EXCHANGE IN ZEOLITES

The most widely studied base-exchanging systems are those of the hydrated alumino-silicates. The various zeolites and silicates are among the most important constituents of the soils, and the permutites or artificial zeolites in particular have been much used
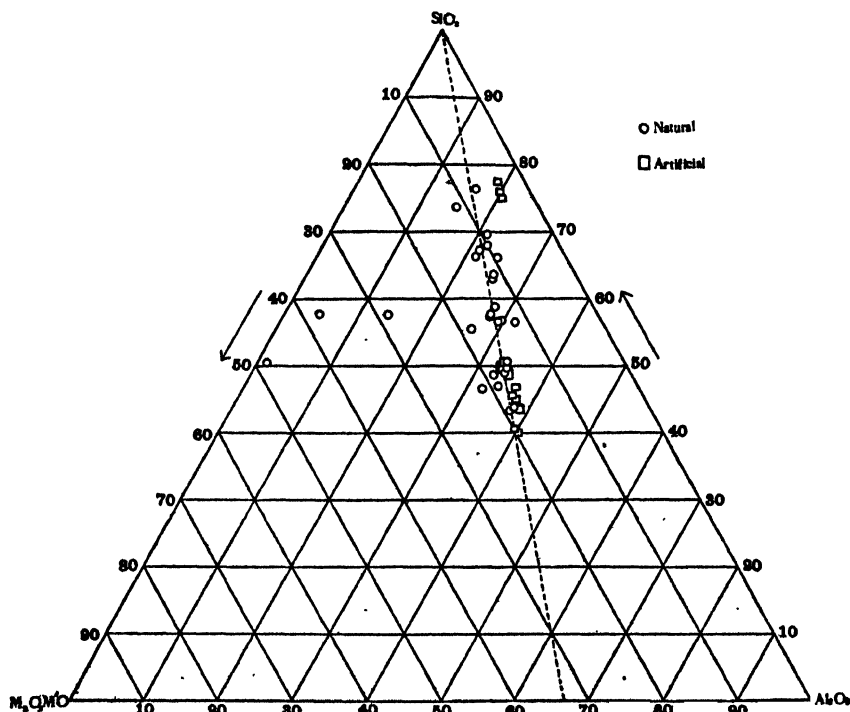
FIG. 1. COMPOSITION OF ZEOLITES

in technical water purification. These substances are classed as insoluble in water, and many of them are usually referred to as colloids. We shall summarize the principal communications relative to the properties of the zeolites, their composition and the theoretical explanations which have been proposed to explain their properties and shall finally indicate the way in which the foregoing point of view can be applied to these interesting substances.

Analyses

From the analyses of twenty-seven natural zeolites (27) given in the literature, we find a very definite, constant alkali-akaline earth to aluminum oxide ratio. We have shown this graphically by plotting these analyses, calculated in mole percents, in figure 1. It will be noticed that only three of these twenty-seven points lie out of the immediate vicinity of the other twenty-four. At least two-thirds of the points lie on, or else very close to the dotted line, which we have drawn to show this relationship. There is a considerable variation in the ratios of alkalies to alkaline earths, which indicates that there is no such definite relationship as we find in the alkali-alkaline earth to aluminum oxide ratio.

The analyses of thirteen artificial zeolites (28), also shown graphically in figure 1, show the same constant alkali-alkaline earth to aluminum oxide ratio. Burgess and McGeorge conclude that zeolites are true chemical compounds, that they have a definite solubility and are capable of ionization.

Methods of preparation of artificial zeolites

A great many patents have been granted in Germany, Great Britain and the United States for the manufacture of artificial zeolites. Many of them are essentially the same, although slight variations occur. In general, the process consists of fusing together an alumina mineral, aluminum silicate, or aluminate, and an alkali and alkali carbonate with a sufficient quantity of an inorganic salt, preferably a borate, to ensure that on the extraction of the melt with water, there will remain only *crystalline* hydrated aluminum silicates (29). Frequently quartz or rocks rich in quartz are added, the proportions being so regulated that *no* free alkali or alkali carbonate is contained in the molten product (30). The transparent crystals or lamina obtained readily exchange their bases. It is planned that all the alkali shall combine with the Al_2O_3 and SiO_2 so that no gelatinous silicates or aluminates form when water is added (31).

Hydrous aluminum silicates are obtained when (32) a mixture of sodium sulfate and carbon is substituted, in the fusion process, for the alkali carbonate or soda. The sodium sulfide formed com-

bines with the silicic acid to form a sodium silicate. Sometimes the molten mass is broken up and subjected to the action of steam under pressure (33).

Occasionally products of approximately definite composition are obtained. If 2.5–3 parts of kaolin, 5–6.5 parts of sodium carbonate and 1.5–2.4 parts of borax are mixed together, the mixture fused, and the melt extracted with water, a product with the approximate formula $3SiO_2 \cdot Al_2O_3 \cdot Na_2O$ is obtained (34). This product may be used for removing soda and potash from saccharine juices or for purifying water. Another similar mixture consists of 56 parts of sodium carbonate, 12 parts of kaolin and 6–7 parts of potassium carbonate (35). After fusion, this forms a glassy melt which is crushed, the alkalies are dissolved out with hot water, and then the mass is recrushed.

Sometimes zeolites are formed by mixing solutions of alkali aluminate and alkali silicate, with the addition of sodium sulfate and sodium chloride, and then heating the mixture to the boiling point (36). The bulky precipitate is separated, washed, dried and calcined. (The aluminate solution is obtained by adding sodium hydroxide solution to a solution of an aluminum salt until the precipitate first formed redissolves.) This process is called the wet method, and usually employs very dilute solutions of the reagents (37). An example mentions 6 lbs. Na_2SO_4, 12 gals. H_2O, 844 cc. of a solution of alumina containing 45.6 grams Al_2O_3, and 315 grams of water glass solution at 45° Be′ containing 75 grams of SiO_2. The precipitate obtained is washed, dried into a cake, broken up and hydrated in hot water.

One of the recent methods consists in forming the mixture so that there are two moles of CaO to each mole of SiO_2 (38). There is also added alkali metal hydroxide or carbonate to bring the ratio of alkali metal oxide to a point above an equivalent molecular proportion based on the alumina present. When the product is taken from the furnace, it is leached with a solution containing several moles of alkali for each mole of alumina present. The recovered alumina and other products obtained from the furnace may be used as fertilizers.

"Doucil" is prepared by mixing at a temperature below 20° a

dilute solution of sodium aluminate and neutral sodium silicate (39).   The product contains 6 to 16 per cent of alumina depending upon the conditions.   One cubic foot will soften a thousand gallons of water containing ten parts of calcium oxide per one hundred thousand.   Four pounds of sodium chloride per cubic foot of material are required for regeneration.   It is guaranteed that 5 per cent of the dry weight of the material can be exchanged for calcium compounds.   Experimental work gives values of 7 to 8 per cent.

Artificial zeolites which have been used for softening water (so that their Na has been replaced by Ca and Mg) are regenerated by treatment with a solution of sodium chloride (40).

Water absorption and dehydration

There has been much discussion about the manner in which water occurs in zeolites.   Panichi (41) maintains that ultramicroscopic observations indicate the crystalline character of zeolites. He measured the extinction angles under varying temperatures and accurately determined the loss of water on heating.

Zambonini (42) claims that zeolites are "solid solutions". Rothmund (43) allowed samples to stand for an hour over 1.0 N H_2SO_4 until they took up a definite quantity of water.   They were then heated at a definite high temperature for 30 minutes and hydrated as before.   The initial temperature was 100°; it was raised 50° each time and continued up to 1000°.   Thus the temperature at which loss of water becomes irreversible was determined.   Zeolites vary as to the temperature at which they cease to be reversible with respect to loss of water.   With silica, the water absorption is reversible only in a certain range, while with sodium permutite it is not really reversible under those conditions. Rothmund believes that there is a strong possibility that the water is held in "solid solution".

van Bemmelen (44), working with silica gel, states that its dehydration is not due to transitions of hydrates, but to physical changes in the structure of the gel.   There is a point in the dehydration where the "volume" of the gel no longer decreases; at this point pores appear, causing opaqueness; at a further point the

opaque mass again becomes transparent. Characteristic points occur at various concentrations and vapor pressures, depending on the manner of preparation and age of the gel, the velocity of dehydration and the temperature.

Zeolites formed at lower temperatures (45) are richer in water (in molecular proportion) than those formed at higher temperatures. The zeolites in general differ from the other hydrous silicates in that their water content depends upon the fineness of subdivision, atmospheric conditions, etc. (46). For this reason, marked variations are found in their analyses. Natrolite was examined. On account of the presence of fluoride, on treatment with hydrochloric acid a part of the silicon escaped as silicon fluoride, giving low figures for silica, and the divergence in published analyses no doubt results from failure to take this fact into account. Of twenty-four other zeolites, all showed 0.4 to 4.0 per cent increase in water content on fine grinding. Upon this basis, he regards water as being chemically combined, since it appeared to obey the laws of definite proportions. The difference between the zeolites and the so-called true hydrous minerals was assumed to lie in the fact that the former have the same crystal form in both hydrous and anhydrous condition, so that on heating they do not disintegrate, as do the latter.

Vapor pressure measurements were made by Löwenstein (47) at temperatures varying from 24.5° to 26°. The material consisted of crystalline hydrates which remained clear during dehydration. These natural zeolites lost varying amounts of water. Substitution of their calcium by potassium (by digesting the powdered mineral for about 100 hours at 100° with frequently renewed 10 per cent potassium chloride solution) caused a decrease in the amount of water present but an increase in vapor pressure for the same water content. Treating these potassium zeolites with calcium chloride solutions, artificial calcium zeolites were obtained which proved, as regards their water content and vapor pressure, to be identical with the original zeolites within the experimental error.

Different specimens of hydrated silicic acids showed different vapor pressures for the same water content. It could not be

determined whether this was due to chemical differences or to differences in colloidal state. There were no discontinuities and hence no definite hydrates.

Grandjean (48) found that zeolites, after dehydration, absorb considerable quantities of ammonia, hydrogen sulfide, alcohol and sodium silicate. Absorption of iodine, bromine, calomel, mercury, sulfur and cinnabar caused marked changes in optical power, e.g., a large variation in optical angle, birefringence, and even a change in double refraction.

An artificial gel—a so-called potash permutite—was extracted with potassium chloride solution by Rostworoski and Wiegner (49) until no more calcium could be removed. The resulting permutite was washed with distilled water until free of chloride ions. The potassium permutite thus prepared had the normal power of exchanging bases, potassium for ammonium, etc., but, from solutions of phosphate in the forms of KH_2PO_4 and K_2HPO_4, or KH_2PO_4 neutral toward phenolphthalein with potassium hydroxide, there was no appreciable absorption of phosphate.

Gédroitz (50) found that the quantity of base absorbed in soils, but not "the energy of absorption", depends on the nature of the cation. "Absorption energy" was greater with trivalent than with bivalent cations, and still less with monovalent cations. Calcium was absorbed more energetically than magnesium, and potassium than sodium. The zeolitic part of alkali soils was richer in sodium than in calcium.

Gédroitz (51) looks upon the retention of dispersed substances by soil grains as mechanical adsorption, while the exchange of cations from solution is looked upon as a purely physical process which takes place on the *surface* of solid particles. He considers the exchange of bases to take place in complex alumino-silicates. Ammonium chloride solution of a concentration of 1.0–4.0 N was necessary for complete instantaneous base exchange. Physically adsorbed substances will be leached out, while those physico-chemically adsorbed will be retained so that the total concentration of the solution is not changed.

Structure of zeolites

Baschieri (52) considers zeolites to be salts of ortho-silicic acid, of meta-silicic acid, and of di-silicic acid (53), while Löwenstein (47) considers them salts of various hydrated silicic acids. Thus, different specimens showed different vapor pressures for the same water content. He could not determine whether this was due to a chemical difference or to a difference in colloidal state, because no discontinuities were observed. Consequently he concluded that the zeolites were not definite hydrates. On one hand, Gans (54) maintains that zeolites are definite chemical compounds and not adsorption compounds, on the ground that the Freundlich formula yields a constant with zeolites but should not do so with adsorption compounds. On the other hand, Wiegner (55) concludes that they are adsorption compounds because he found the displacement in hydrated amorphous silica gels in close accord with equations for adsorption reactions. Wiegner (56) also gives the explanation that the colloidal compound of aluminum hydroxide and silica, charged positively through the aluminum hydroxide, has a strong adsorptive power for OH^- ions. He considers the cations in equivalent quantities concentrated in the gel water. These gels, containing these bases in the gel water, constitute the "double silicates with replacement power." The gel is thus in adsorption equilibrium with reference to OH^- ions when in contact with water and supersaturated with cations, held electrochemically in the gel water. The cations, entering into the capillary spaces of the gel, displace equivalent cations. If the capillary spaces of the gel are reduced through partial dehydration, then the replacement power is reduced; and if the gel is fused, then there is no more replacement.

There have been attempts made to assign definite formulas to zeolites. Tschermak (57), from the analyses of twenty-one different zeolites, states that in all cases the ratio $(Al)_2[Ca(Sr, Ba) + Na_2(K_2)]$ exists; and that if he omitted the oxygen, all zeolites had formulas represented by $Si_xAl_2CaH_{2y}$ and $Si_zAl_2Na_2H_{2v}$, where x and z range from 2 to 10, and y and v from 2 to 9; or, neglecting the hydrogen, they all contained a group $Si_2Al_2CaO_8$ or $Si_2Al_2Na_2O_8$. This latter group he regards as the nucleus. The

various zeolites are regarded as compounds of one or other of these nuclei with a silica acid, combined water and water of crystallization. The silicic acid and water of hydration are supposed to form a network enclosing the nuclei. Such a structure he regards as offering explanation for the variation of the optical characters of the zeolites with loss or gain of water, the various adsorption phenomena and the ease with which the bases may be replaced. Scurti (58) in maintaining that zeolites are salts of a series of alumino-silicic acids, states that some of the acidic hydroxy groups are attached to silicon and some to aluminum, thus explaining amphoteric properties. He relates the acidity of soils to the number of hydroxy groups attached to silicon in comparison with the number attached to aluminum.

Leitmeier (59) discusses the relations of colloidal and crystalline substances. There is great difference of opinion as to whether clay minerals are gels or definite chemical compounds. Gels of SiO_2 and Al_2O_3 change to crystalline forms with extreme slowness. Winchell (60) states that zeolites form a number of isomorphous series, and that in any one series, variations may occur so that in each series Ca + 2Na (atoms) is a constant; also that the Al_2O_3:CaO ratio is unity for all zeolites and that the ratio of (Al + Si):O is always 1:2. Only a few exceptions occur.

Weigel (61) pictures a very definite structure for zeolites. He states that in their formation, where the silicate particles have assumed a comparatively rigid lattice orientation, the solvent, in which the crystals form, remains within the lattice meshes, without, however, contributing to the lattice structure. Energy is lost through overcoming the internal pressure of the solvent, and this energy aids in the erection of the lattice. The latter retains its rigidity under various conditions, and the energy of the internal pressure is free and serves to bind foreign substances. The ready exchange of bases is explained by weakened bonds in the silicate lattice. He expresses the relation between temperature, the vapor pressure of the surroundings and the amount of adsorbed foreign molecules by a modified van der Waals' equation:

$$n = n/b - [R(T - T_s)v^2]/[a(v - nb)]$$

where n is the number of adsorbed molecules in a silicate molecule, R is the gas constant, T the absolute temperature, T_s the temperature of the saturation pressure of the liquid phase of the foreign substance which itself is at temperature T in the medium surrounding the crystal, a the van der Waals' constant of the medium in which the zeolite forms at the temperature and pressure involved, and b a constant. Weigel has shown that the equation has, within certain limits, given results conforming well to the experimental material available. Ridley (62) considers silicates to be 10- or 12-membered rings of alternate silicon or aluminum and oxygen atoms. Rothmund (63) has recently expressed the opinion that zeolites hold water in the same way as gels and not as hydrated salts, since the water molecules take no essential part in the crystal structure.

Base Exchange

Much has been written about base exchange in zeolites. The idea can be traced (64) from Way's original papers in 1850 through the various commercial and industrial applications. In studying the subject, it is necessary to know the properties of both the simple silicates and the alumino-silicates. Thus Gans (65) found that silicates obtained from material extracted from soils by dilute hydrochloric acid resembled zeolites in replacement of their bases by salt solutions, their behavior towards boiling water, higher temperature, lime and soda. Consequently he divided zeolites into two classes, namely (1) those which very readily exchange their bases and (2) those in which the exchange takes a long time.

In Gans's first class the bases are united only to the aluminum; thus the silicic acid is combined with such groups as Al(OH)-(ONa) or Al (ONa). In the second class the bases are united directly to the silicic acid. He made artificial products of the first class by the action of alkali aluminate on hydrous silicic acid, silicious sinter, infusorial earth, etc., or on the alkali silicate solution. A product of the second class was prepared by the action of an alkali silicate on aluminum hydroxide. He calls the first class the aluminate-silicate-zeolites; the second class the alumina-

double-silicate-zeolites. The first group rarely occurs pure in nature. The Al-free apophyllite does not exchange its bases in a short time; they are therefore united to the silicic acid. He places zeolitic compounds of arable field soils in the first group. Concentrated ammonium chloride solutions were found to exchange the bases of the finely ground zeolites of the first class in two days, while no bases of the zeolites of the second class went into solution. The two classes are formed by the mingling of the decomposition solutions of alkali aluminates and alkali silicates, or through hydration of aluminum silicates. If carbonic acid is absent the aluminate silicates of the first class form, otherwise those of the second class or mixtures of the two, because alumina is precipitated by carbonic acid. The first class is of great technical importance, as zeolites of this class are capable of exchanging their lime for the alkali and trimethyl glycocoll content of molasses and therefore permit of an increased crystallization of sugar. By the action of calcium chloride solutions the alkali aluminate silicates can be changed to calcium aluminate silicates.

Zoch (66) shook zeolites in solutions of ammonium chloride. He found the reaction at first comparatively rapid although equilibrium was reached only slowly. Thus with stilbite in grains of 0.25–5 mm. diameter equilibrium was reached after forty to fifty days. Temperature, fineness and quantity of powder, and strength of solution all exert an influence. There was an exchange of the bases calcium, sodium and potassium only, these being replaced by an equivalent amount of ammonium. Alumina and silica did not pass into solution, and the amount of chloride in the latter remained constant. Substitution was accompanied by change in optical characters of the material.

The reaction of powdered chabazite specimens with 0.1–0.66 N alkali chloride solutions was studied by Reiner (67) at 13° and 60°. Base exchange was indicated by the liberated calcium. The data obtained show the effect of heat and of concentration of solution in promoting base exchange. In order of their ability to replace calcium from the mineral, the alkalies are potassium, ammonium, sodium and lithium. Desmine, in which half of the calcium was replaced by potassium, reacted somewhat with silver

nitrate solution.   A slight break in the time-reaction curve occurs when the bases reach the ratio $CaO:(K_2O + Ag_2O) = 1.2$.   Under the influence of Roentgen rays, the reaction ended in thirty minutes, although it was less than half complete.   Without these rays, the reaction went more nearly to completion, if at all, but only after ten or more days.   Reiner postulated the formation, by the rays, of ions in the mineral which do not exchange bases.

In separating zeolitic powders in potassium mercuric iodide solution, Walker (68) found several were attacked with nearly complete replacement of the original sodium by potassium. Thus a gmelinite separated by organic liquids gave $Na_2O = 10.08$ per cent and $K_2O = 0.69$ per cent, while the same mineral separated as above gave $Na_2O = 1.20$ per cent and $K_2O = 14.86$ per cent. Okenite, originally containing 0.60 per cent K_2O showed, after the separation, 2.24 per cent.   Some irregularities in published zeolite analyses may have been due to reactions having occurred with separating solutions.

Analyses were made by Hulbert (69) of three commercial zeolites under exactly identical conditions; first when regenerated with sodium chloride, and again when sufficient magnesium sulfate solution was passed through the silicate to bring about the most complete exchange or replacement of sodium by magnesium. The experiments were repeated with calcium chloride, and definite relative capacities of the zeolites for exchange of different ions was established.

Vogtherr (70) concluded that the active exchangeable bases are embedded in the porous structure of the zeolites, in whose fine capillaries the exchange action takes place.   He thought that the silicate itself, whether composed of silica alone, or in combination with alumina or iron oxide, did not play any function in the exchange of bases except to furnish a medium of suitable physical nature.

Base exchange in permutites is believed by Wiegner and Jenny (71) to depend upon ionic interchange and in turn upon the hydration of the ions in solution.   They found a definite relation between the exchange and the atomic volume of the ions.

Adsorption studies by Ramann (72) show that quartz adsorbs

alkaline compounds strongly, but neutral salts and acids in traces only. Base exchange studies with permutite by Ramann (72) indicate that the exchange is always in chemically equivalent quantities. The more easily a metal is taken up, the more difficult it is to displace it. Ions were taken up in the following order: $Mg < Li < Ca < Na < Ba < NH_4 < K < H$. With alkaline solutions, an absorption of bases in addition to the exchange occurs. The exchange of hydrogen ions for neutral salts was incomplete.

Frankforter and Jensen (73) made a series of preliminary experiments to determine the mechanism of the exchange reactions taking place when an alkali metal zeolite or permutite is treated with an alkaline earth metal, or *vice versa*, using aqueous solutions of sodium, calcium and barium chlorides of various concentrations. A large excess of the replacing metallic ion was necessary for complete exchange. Barium showed approximately 4.5 times the replacing power of calcium when both were present in equivalent amounts. Exchange reactions were more nearly complete with dilute than with concentrated solutions, an observation they take to indicate that these reactions are ionic.

Equilibria in solutions of two salts of varying concentrations when shaken with permutite containing the same cations as the solution, were investigated by Günther-Schulze (74). This was done with the object of ascertaining the concentration of the solution which is in equilibrium with the permutite. The experiments were carried out at 22° with 50 per cent silver and 50 per cent ammonium, 33.33 per cent copper and 66.67 per cent ammonium, 4 per cent lanthanum and 96 per cent ammonium permutites. All the solutions contained the respective salts as nitrates. The results show that to a certain extent the demands of the law of mass action are fulfilled.

Copper chloride, acetate, formate, sulfate, chlorate, nitrate and bromide solutions were also investigated (75) by shaking known concentrations of the salts with pure potassium permutite. From measurements of exchange of cations between the permutite and the solution he drew conclusions as to the presence of complexes in the solution. Thus, even at greatest dilution the simple complex cation CuR^+ was assumed present in practically all of the

copper salt solutions examined. The presence of the complex $Cu_2R_3^+$ was considered proved only in the case of the copper chloride and bromide. He thought it probable that the other salts exhibit the higher complex formation, which, however, is not present to such a great extent. The complexity of copper salt solutions increases at constant concentration with the strength of the acid, and is greater with the salts of halogen acids than with the salts of oxygen acids of equal strength. His data may, however, be interpreted in a much simpler manner.

Interchange of bases, occurring in mixed solutions containing two different bases, has been studied by Ramann and Spengel (76) by means of a permutite of moderately constant composition prepared in the wet way. The replacement of bases taking place when such a hydrated aluminum silicate was treated with neutral potassium, ammonium, calcium and sodium salts had the character of a chemical change, no signs of physical adsorption being detectable. The interchanges were by equivalents, that of potassium and ammonium following the law of mass action. The curves expressing the ratios of the ions in solution and those of the bases in the silicates are coincident. In solutions containing sodium and calcium salts, the interchange of bases corresponded predominantly with the ratio of the ions in the solution, but preponderance of the calcium or sodium salts resulted in divergences dependent upon a second factor of unknown nature. Potassium and ammonium were mutually replaceable, and displaced sodium and calcium completely from the silicate; whereas the displacement of potassium and ammonium by sodium and calcium was incomplete. The ratios between the bases in the solutions and in the silicates have different values. Bases present in small proportions in the solutions were combined by the silicate in amounts greater than those corresponding with such proportions. Within wide limits the absolute concentrations of the salts in the solution are without appreciable influence on the composition of the silicate, this being the case even with mixtures of calcium salts with those of the univalent metals.

Kornfeld (77) found that shaking for twenty minutes was sufficient to complete the interchange of sodium in sodium permutite

by silver, and of silver in silver permutite by potassium, barium, and ammonium. In all cases except the replacement of silver by barium, the concentration of the solution had no effect on the amount of change. The change between sodium permutite and silver is represented by the equation

$$[Ag \text{ (in permutite)}/Na \text{(in permutite)}]^{1.44} \times c(Na^+)/c(Ag^+) = 129$$

In the case of silver permutite and ammonium nitrate, the reaction is represented by

$$[Ag \text{ (in permutite)}/NH_4 \text{ (in permutite)}]^{1.67} \times c(NH_4^+)/c(Ag^+) = 37.7$$

The replacement of silver by potassum is given by the equation

$$[Ag \text{ (in permutite)}/K \text{ (in permutite)}]^{2.17} \times c(K^+)/c(Ag^+) = 9.9$$

and the replacement of silver by barium by the formula

$$[Ag \text{ (in permutite)}/Ba^{\frac{1}{2}} \text{ (in permutite)}]^{2.3} \times c^{\frac{1}{2}} (Ba^{++})/c(Ag^+) = 1.5$$

Rothmund and Kornfeld (78) also found that when the finely powdered solid is shaken up with a salt solution, the replacement of the cation by some other cation reaches an equilibrium in less than ten minutes. They considered the reaction to be chemical and not merely adsorption. Experiments were carried out with silver and sodium permutites and the nitrates of sodium, potassium, rubidium, lithium, ammonium, thallium, and silver. If c_1 and c_2 represent the concentration of the bases in the solution and c_1' and c_2' in the solid permutite in equilibrium with the solution, it is shown that some power β can be found so that the ratio

$$(c_1/c_2)/(c_1'/c_2')^\beta = K$$

where K is a constant. The value of β is generally about 0.5.

Rothmund and Kornfeld (79) also examined bivalent and trivalent ions. The theoretical relations previously derived for uni-univalent interchange, and extended to other types, are confirmed in these cases, also, both for bi-bivalent and for uni-bivalent interchange.

In the case of silicates, present in the soil, relations analogous to those in permutites are discussed by Ramann (80). Thus the replacement of the bases by alkalies and by ammonium is

assumed to depend upon ionic reactions: equivalent quantities of the cations are introduced into the permutites independent of the nature of the anion present in the solution. The composition of the permutite at the end of the reaction was found independent of the total concentration of the solution.

The ammonium in ammonium permutite can be replaced by other bases by treatment with solutions of salts. Ramann and Spengel (81) found that when sodium and potassium were the bases used, the resulting product containing sodium, potassium, and ammonium in the ratio of the corresponding ions in the solution; but when calcium was present the exchange as regards this base did not comply with this simple law.

The decomposition of natural silicates, which cannot always be adequately accounted for by the action of water and carbonic acid, was thought by Ramann and Junk (82) to be related to the following. The reaction, in the formation of magnesium permutite by the action of magnesium salts on ammonium, sodium and potassium permutites, is ionic; and there is no evidence of physical adsorption. Pure magnesium permutite could not be obtained, not more than half of the bases present in the original permutite being displaced by the magnesium. The whole of the ammonium in ammonium permutite could not be displaced with carnallite or kainite solution. Mixed salt solutions decompose the permutite to some extent, especially solutions containing magnesium or ammonium.

THE ZEOLITE AS A MICELLE

In a previous section, we saw that the activity coefficient of a micelle decreases as the number of ions aggregating to form the micelle increases. In the limit, if all the ions, for instance the negative ions, in a given solution, combine to form a single micelle, then an extension of our ideas of the properties of an electrolytic solution predicts that the activity coefficient of such a micelle is nearly zero. In other words, the micelle still retains the characteristics of an electrolyte in much the same way that a typical crystal retains the properties of an electrolyte. Perhaps it is only a point of view which distinguishes the ordinary conception of a

solid solution from that which we are presenting. The same thermodynamic requirements are maintained. However, the viewpoint here taken allows us to consider systems which come rapidly to equilibrium only on the surface of the solid. Because the ordinary processes of diffusion in a crystalline solid are slow, the actual attainment of equilibrium throughout a solid is also slow.

The rate of attainment of equilibrium of the zeolites with the solutions with which they are in contact is rapid, but the zeolites after many cycles of base exchange, in the presence of small amounts of carbon dioxide, gradually lose their efficiency. Furthermore, as we have seen, the ratio of the bases in the liquid phase to the bases in the solid phase is not always constant but varies with the method of manufacture of an artificial zeolite or the method of deposition of a natural zeolite.

Zeolites and related substances are all salts of alumino-silicates. Let us assume that the negative ions of the alumino-silicate form large micelles, and that the constraints between the atoms are large. The substances would therefore behave as very viscous liquids or as glass-like solids. The positive ions, because of the rigidity of the system, are held tightly to the micelle in order to maintain the electro-neutrality of the system.

We will assume that the zeolite has been treated with a concentrated solution of sodium chloride so that the only positive ions present on the surface of the micelles are sodium ions. If now a new solution of calcium or ammonium chloride is substituted for the sodium chloride, the ratio of sodium to ammonium ions in the solution to sodium to ammonium in the zeolite becomes a constant for the particular sample of zeolite.

The natural zeolites show all the optical characteristics of definitely crystalline substances. On the other hand, the artificial zeolites, from their method of preparation, would appear to have more of the character of amorphous substances. The individual micelle or ramifying aggregate of micelles may have a more or less regular lattice arrangement. The tendency, as we have seen, is to regard these natural and artificial zeolites as compounds of different composition, or at least as solid solutions of a number of definite chemical individuals, such as calcium alumino-silicate and sodium alumino-silicate, etc.

When an artificial zeolite is prepared by mixing sodium aluminate with sodium silicate in different proportions, there usually results a complex sodium alumino-silicate which approaches the same composition as that of natural nephelite, i.e., the composition of the zeolite differs little whether a small or large amount of sodium aluminate is employed, except that with a large amount the firm gel forms instantly. However, all alumino-silicates with wide variation in ratio of silica to alumina show the base exchange property.

In figure 1 we showed the composition of various natural and artificial zeolites. Their capacity for base exchange depends not so much on the composition as upon their "history." In the formation of zeolites, we therefore think of the process as being one in which the aluminate and silicate ions, because of their electron affinity, react to form very strongly micellar-forming acid ions. The positive ions are then bound to the multi-charged ionic micelle in order to maintain electro-neutrality in the immediate vicinity of the large charged mass. And while there may be a real orientation of the atoms in the most efficient base-exchanging zeolites, these positive "held" ions must be in such a position that they are readily diffusible into a solution in which the micelle is placed. The variability of the composition of the zeolite supports this view.

Biesalski (83) found that pure acid-silicate grains (84) containing high proportions of silica,—(a) SiO_2 90.1 per cent, Na_2O 3.0 per cent; loss on heating 7.3 per cent; (b) SiO_2 85 per cent, Na_2O 4.4 per cent, loss 10.6 per cent; (c) SiO_2 75.3 per cent, Na_2O 3.8 per cent, loss 20.1 per cent—possessed the property of base exchange. These sodium silicate grains contain so high a proportion of silica that they are either insoluble or extremely slowly soluble. The probability of the micellar character of these highly silicious hydrous sodium silicates is indicated by the discussion in a previous paper (3e).

Biesalski (83) also studied complex sodium silicates of the type in which zinc replaces the aluminum in a zeolite (85), SiO_2 35.4 per cent, ZnO 20.0 per cent, Na_2O 10.7 per cent, loss 33.8 per cent. He found base exchange properties. These experiments indicate

that the base exchange property of the zeolites is not necessarily a property of the alumino-silicate but more of the silica, which we have seen has the property of forming electrolytic micelles (3f). In the grains these micelles are rigidly fixed, but this inability of the micelle to take part in a Brownian movement does not alter the character of the base exchange process. The tendency noted in figure 1 for the alumino-silicates to form with a constant ratio of replaceable base to alumina must be related to the chemical character of the aluminate.

Zeolites usually lose their base exchange properties upon the repetition of the base exchange cycle. This is ordinarily explained on the basis of the hydrolysis of the zeolite, which process, indeed, we saw (3f) to be operative in the case of the pure sodium silicates. This hydrolytic process is hastened by acids, even as weak as carbonic acid, competing for the base ion equivalent to the hydroxyl ion formed by the hydrolytic splitting of a part of the micelle.

With the definitely crystalline zeolites, there is no constant ratio between the ratio of the activities of the base ions in the solution and the ratio of the bases in the zeolites. If we substitute the ratio of the activities of the bases in the solid solution of the zeolite, such constancy must exist if sufficient time to reach equilibrium throughout the solid mass is given. The viewpoint of the electrolytic micelle merely focuses our attention upon the easy metathetical exchange characteristic of ionic reactions.

We have mentioned the specificity of the binding of positive ions to a micelle such as that postulated in the case of the insoluble soap. It is obvious that that portion of the decrease in the activity coefficient which is due to the "association" in the Bjerrum sense must be specific; and hence arises the reason for the ratio of the concentrations of the salts in the solution being different from their ratio of existence in the micelle. In looking at this in another way, we might say that the solubility of calcium alumino-silicate is less than that of sodium alumino-silicate, while, from the viewpoint of micellar formation we would say that the activity coefficient of the calcium micelle is less than that of the sodium micelle. But this does not preclude the possibility that

both calcium and sodium ions may be adjacent as contributors to the electrical neutrality of the small micellar particle. We are here trying to unify the ideas of the adsorption theory and those of the chemical theory. We take the crystalline zeolites as examples of micelles of very large numbers of atoms.

SUMMARY

Micelles are considered as the intermediate steps between ordinary ions and solid crystals. The solution of micelles is taken as a homogeneous phase, and the thermodynamics of such a system is therefore that of the homogeneous phase rather than that of the heterogeneous system.

In this paper the following topics have been discussed:

1. The consequences of the extension of the theory of the formation of micelles when very large aggregates are formed.

2. The electrolytic nature of crystalline and near crystalline micelles. The activity coefficient of such crystalline micellar masses is practically zero.

3. The relation of complexes and micelles.

4. The rapid base or acid exchange properties of solid solutions and of zeolites. This is explained by the electrolytic nature of the solids.

5. Base exchange in other systems.

6. Base exchange in zeolites.

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THE SUBSTITUTION OF LINKED AROMATIC RING SYSTEMS

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General interest in the experimental investigation of the substitution reactions of chemical molecules containing more than one aromatic ring system may be traced back to 1912, when Cain, Coulthard and Micklethwait (1) announced that two distinct dinitrobenzidines could be obtained by nitrating acyl derivatives of benzidine. By analogy with the known reactions of aniline, there should have been produced, instead of these two isomers, but one substance—3, 3'-dinitrobenzidine. Unfortunately, the correct elucidation of this discovery was delayed for several years, owing to the proposal of a stereochemical explanation of the isomerism which, though incorrect, served to divert attention from the actual question of the mode of substitution of more complex aromatic compounds.

Since 1920, however, the very rapidly increasing number of experimental studies has shown clearly that the early empirical rules for the classification of substitution-directing groups—such as that of Crum Brown and Gibson—are inadequate guides for the prediction of the courses of substitution reactions. Also, following the application of the newer electronic theories of valency to organic chemistry, it has been realized that the explanatory theories of aromatic substitution must be based essentially upon experimental facts of unquestionable validity and not upon deductions based on analogies and statistical schemes of correlations. Consequently the field of investigation has been widened, and the substitution reactions of such complex aromatic compounds as diphenyl, benzophenone, phenylpyridine, and other substances containing more than one aromatic ring linked

up within a single molecule, have become worth experimental study.

Though the as yet recorded observations of the substitution reactions of compounds having the general type of figure (I), in which two *independently complete* aromatic rings (A) and (B)

$$R-\langle\ A\ \rangle-X-Y-\langle\ B\ \rangle-R'$$
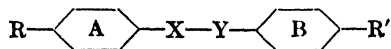
(I)

are linked together by any grouping or assemblage of groupings $(-XY-)$, are very scattered and incomplete, they have already attracted considerable attention in one or two instances, notably in the cases of the diphenyl and phenylpyridine series.   It should be noted that only with compounds of type (I) is it possible to ensure that comparisons of the reactivities of the two different aromatic nuclei (A and B) are made under absolutely identical experimental conditions.   Whatever types of reactions are carried out with such "binuclear" substances as these, both rings must remain equally affected by the many possible external influences, such as those due to the substituting reagent, to the solvents employed, or to the catalysts which may be present.   No such certain elimination of differential external effects, which might arise through mere differences in solubility or in degree of solvation, can be attained when two different aromatic molecules are compared, even if these are mixed together before treatment with a common substituting reagent, as has been done in several recent researches (2, 3).

It is the object of this article to correlate the experimental results recorded throughout the whole wide field of investigation outlined above, and to discuss their general characteristics in terms current in modern theories of aromatic substitution.

Several different characteristics of aromatic substitution can be studied with the aid of linked ring systems, according to the actual types of compounds chosen for investigation.   With simple compounds like diphenyl, or benzophenone, one can examine first the degree of reactivity and the mode of direction of substituting groups in any one ring (A) produced by the other ring (B),

acting of course in combination with the linking group $(-XY-)$.
When this linking group is unsymmetrical—as in benzoin—it
will induce different reactivity effects in the two rings. These
can be differentiated from each other and compared directly
with great ease. Consequently one can study the effect of
systematic variation of any divalent group $(-XY-)$.

In more highly substituted linked ring compounds, of the type
actually formulated in figure (I), further effects due to the other
substituent groups $(-R)$ and $(-R')$ can be traced. The com-
pound (I) can be analyzed as if made up of two substances (II)
and (III),

R—⟨ A ⟩—XY—ϕ_1 ϕ_2—YX—⟨ B ⟩—R'

(II)   (III)
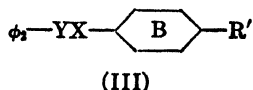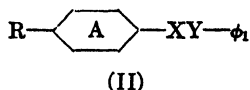
each containing an aromatic ring in which substituent groups may
compete in controlling the mode of substitution. Since any sub-
stance of type (I) may also be regarded as a substituted linked ring
compound, it may be anticipated that valuable results may be
obtained by studying the reactions of highly substituted aromatic
compounds.

In all "linked ring systems" effects may be traced which are due
not only to the special properties of the substituent groups (R
and R') or linking groups (X and Y), but also to the ring systems
(A and B) themselves. Reactivity in ring (B) may be induced or
inhibited by special influences from the aromatic ring (A) that
are transmitted either through space or through the linking groups,
and comparisons may be made of the relative actions of the vari-
ous linking groups $(-XY-)$ in assisting or in hindering this
transmission.

Linked ring systems can therefore provide data for the system-
atic comparison of several of the more important factors influenc-
ing aromatic substitution.

Modern explanations of aromatic substitution, even when
applied to the simplest of benzene derivatives, all involve the
recognition of at least two distinct electropolar influences, apart
from the possibility of the intervention of the geometrical effect

known as "steric hindrance". Dual substitution influences can also be discerned in all these more complex compounds, so that before one can proceed to the explanation of experimental results, it is necessary to differentiate between these polar influences and to trace their separate characteristic manifestations within aromatic rings.

It was first pointed out by Hollemann (4) that the speeds of substitution of different aromatic compounds were markedly different; substances containing *ortho-para* directing groups being more reactive and those containing *meta* directing groups less reactive than benzene itself. This effect has now been recognized definitely as a *general polar action* of the substituent group which is exerted through space and through the intervening atoms in the molecule. Its magnitude can be evaluated in terms of the energy required for ionization at any point of reaction under particular consideration, for a substituent group within any molecule will, in general, modify the electrostatic environment of possible reactive atoms by inducing a definite change in the local electrical potential. By estimating this induced electrical potential in terms of the magnitude of the electrical dipole moment of the directing group, it is possible to get a rough basis of measurement of this general polar effect (5). As Ingold has pointed out (6, 7), this induced electrical polarity may be exerted directly across space, and also relayed successively from atom to atom within the molecule. In certain special cases he has found it advisable to differentiate between these two modes of action, and has named their resultant manifestations the "direct effect" and the inductive effect," respectively. Usually, however, only the resultant sum of these two general polarization effects need be taken into consideration for the explanation of experimental observations.

It is probable that the realization that there can be these two distinct modes of propagation of the "covalency adjustments" of the general polarization effect will attain much significance in the future development of this subject, for, to quote a recent statement by Lapworth (45) in discussing the theory of induced polarization—"Insufficient attention has been paid to the possibility, already partly recognized, that even in the resting state of

a molecule the effect of a substituent at a given point, even at a considerable distance from the substituent, may be the resultant of at least two simultaneous influences, one reaching the point from the exterior and the other from the interior, that is *via* the electronic system of the adjacent atom, the condition of which, in its turn, is likely to be determined by the resultant of interior and exterior influences. The exterior and interior forces at a given point may operate either in harmony or in opposition according to the nature of the substituent, and possibly also according to other circumstances, and obviously may affect one another to a greater or less extent throughout the whole range of collateral transmission."

Theoretical conceptions of the nature of all polarization effects vary very widely, but, whatever conceptual scheme be adopted, there is no doubt at the present time that the *general* polarization effect can be termed an *inductive disturbance.*

General polar influences, primarily altering speeds of reaction, cannot however be used adequately to explain the attraction of entering substituting groups to special points of potential attack in the aromatic molecule. It has been necessary therefore to postulate the existence of an alternating polarity effect, superposed upon the general polarization effect. According to all theories this is regarded as an influence emanating from the "directing substituent group" inducing special reactivity, at the moment of substitution if at no other time, in either the *ortho* and the *para*, or else in the *meta* positions within the same aromatic ring. Recent experimental work (10, 11) seems to indicate that this alternating polar influence can rarely be exerted from outside a single aromatic ring. The effect is probably best considered as an induced tautomeric (or rather electromeric) disturbance (8, 9).

Whatever detailed explanatory schemes be utilized for the description of these two types of induced polar influences, their intrinsic natures can be sharply differentiated as outlined briefly above. The standard nomenclature of Ingold (6, 8, 9) for these effects will therefore be employed throughout the rest of this article, the general polarization effect being denoted by I,

and the alternating polarity effect by T. Except where specifically stated, the general polarization effect, as denoted by I, will be taken as including also the direct effect D.

Evidence obtained from the recorded substitution reactions of linked ring systems, when examined from the modern electronic viewpoint as outlined above, indicates that aromatic rings do very distinctly exert specific inherent polar influences. In brief it may be stated that, though aromatic rings readily permit the transmission of induced electronic movements, involving both the acceptance and the donation of electrons, yet, as far as their own influences are concerned, one consistent type of polar action is to be observed. The aromatic ring therefore does not act merely as a resonator to influences arising elsewhere but also induces electron movements on its own account.

This has been recognized most clearly in the case of the diphenyl ring system, which has been investigated very thoroughly during the past few years (11–15, 36, 40). Although all diphenyl derivatives are completely conjugated systems, in which electromeric polarity transmission (T) might easily occur from ring to ring, yet experiment has shown that not only the unsubstituted phenyl group (C_6H_5) but also *all* substituted phenyl groups (C_6H_4X) have one consistent type of directive action, which is similar to that of all other hydrocarbon radicals (11, 12, 13, 15). Thus, on substitution of all three nitrodiphenyls (figures IV-VI)

NO$_2$—⟨ A ⟩—⟨ B ⟩   ⟨ A ⟩—⟨ B ⟩   ⟨ A ⟩—⟨ B ⟩
                            NO$_2$ NO$_2$
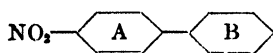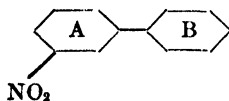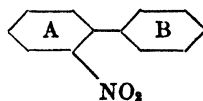
      (IV)   (V)   (VI)

the entering groups invariably attack positions in ring (B) in the *ortho-para* relationship to the nitrophenyl group (A). The same can be stated for substitution in ring (B) when even more powerful orienting groups, like $-NH_2$ or $-OH$, are present in ring (A) (12, 13, 14). Only when the aromatic ring undergoing substitution already contains another substituent group, more powerful in its directive influence than the substituted phenyl group linked to it, can reaction occur at positions in the *meta* relationship to the

bond linking the two aromatic nuclei. This is well illustrated by reference to the acetamidodiphenyls (VII) and (VIII) in which substitution can occur, according to the special experimental conditions, in either of the two nuclei at the positions indicated (12, 14).

(VII)　　　　　　　　　　　(VIII)
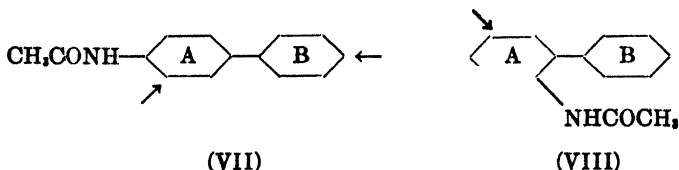
Examination of all other linked ring systems reveals a similar consistency of type of directive action, unaffected by the presence of substituent groups in the ring not actually being substituted.

(IX)
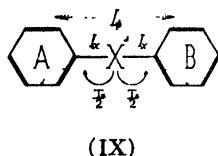
In any compound $C_6H_5-X-C_6H_5$ (figure IX) it is usually impossible for induced alternating electron pulses to be propagated from one ring to another through the linking group $(-X-)$, for, in general, linking groups are not conjugated systems which can undergo the requisite type of electromeric transformation (T) consistent with the preservation of stable electronic groups around each atom. Even in completely conjugated compounds in which internuclear electron movements can and do occur (as, for example, in the case of the cyanine dyestuffs), the alternating polarity influence does not seem to be powerful between the two rings.

Internuclear directive effects have certainly been detected in such compounds as the phenylpyridines (16) though they are not strongly marked, while in such homocyclic systems as diphenyl and azobenzene (17) they have not been found. There may perhaps be an intrinsic difference in the amount of energy required for the sporadic electromeric disturbances (T) which influence reac-

tivity and for those regular, and exceedingly rapid, intramolecular electronic movements to which correspond those absorption band spectra which are so characteristic of all aromatic substances.

In contrast to the restricted range of the alternating polarity influence, general induced electron drifts (I) can be exerted from ring to ring, as they are transmitted, in part at least, through space, and so can only be partly suppressed by the intervening group $(-X-)$. The resultant reactivity of any one ring in a compound (IX) will therefore be influenced by the total $(I + T)_x$ polarization induced by the group $(-X-)$ plus that proportion of the induced electron drift due to the other ring $(I\phi)$ which is transmitted through the linking group. The alternating polarization influence (T_x) exerted by the linking group $(-X-)$, however, will be distributed between the two rings (A) and (B), and therefore will have a markedly different magnitude in either from what it would have in such a compound as figure (X), in which tautomeric electron movement can proceed from $(-X-)$ in one direction only.
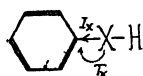
(X)

The general "electron drift" polarization (I_x), induced by the linking group $(-X-)$, if of the nature of an induced electrical potential as has been suggested, will not be so markedly different in the two substances (IX) and (X), for that portion of it which has been characterized as the direct effect (D) should certainly be induced equally on free space or on distant atoms, while the other fraction, transmitted from one atom to the next, should diminish in intensity only with the length of the chain of atoms involved.

When these possibilities of induced polarization are fully taken into account it is found, from collected experimental data, that in all linked ring systems the phenyl group acts uniformly as a powerful "electron source" group with a directive action similar in type to that of the hydrogen atom. It generally increases

reactivity ($+I$), and, when it can originate an activating electromeric disturbance, always induces substitution in the *ortho* and *para* positions in another ring ($+T$). It thus resembles any other hydrocarbon radical, as, for example, the methyl group $-CH_3$ (18).

In illustration of this conclusion it may be pointed out that similar substitution reactions are given by all compounds in any related series ($\phi-X-R$), in which the group ($-R$) may be a hydrogen atom (as in (X)), an alkyl group, or an aryl group (as in (IX)). For example, benzophenone, acetophenone and benzaldehyde are all relatively inert, *meta* substituting compounds, the outer group $-R$ being unable to influence the reacting ring through the intervening carbonyl group. Diphenyl ether, anisole and phenol in contrast are all *ortho-para* substituting compounds with reactivities· differing only in degree according to the extent to which the outer group $-R$ limits the frequency of the activation due to the oxygen atom.

The polar effects due to the outer group ($-R$) are in all cases very slight, but they can be detected quite distinctly by quantitative measurements of directive powers. In such quantitative experiments as have already been carried out it has been demonstrated that an aromatic ring has, in a compound of type (IX), an activating influence ($+I$) of a magnitude very similar to that of the methyl group in an analogous compound of the same general type $\phi-X-R$.

Allan and Robinson (19), for example, have examined the nitration of a series of guaiacol ethers of the type of figure (XI), all of which substitute exclusively in the positions 4 and 5—i.e. in the *para* positions to the groups $-O-CH_2-R$ and $-OCH_3$ respectively.
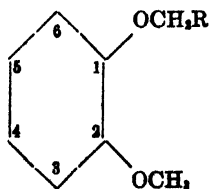
(XI)

From the equation:

$$\frac{\text{Directive power of } -\text{OCH}_2\text{R}}{\text{Directive power of } -\text{OCH}_3} = \frac{\text{per cent of 4 substitution}}{\text{per cent of 5 substitution}}$$

they have been able to obtain fairly accurate estimates of the magnitude of the general polar influence (I) of the group $(-\text{R})$ in modifying the polarization of the oxygen atom of the ether linkage, through which the reactivity is eventually induced. Relative to the directive power of the methoxy group $(\text{R} = \text{H})$ being taken as 100, the directive powers of the methoxy group $(\text{R} = \text{CH}_3)$ and of the benzyloxy group $(\text{R} = \text{C}_6\text{H}_5)$ are respectively 135 and 113. Replacement of the phenyl group by the methyl group, or by hydrogen, has therefore but little effect on the magnitude of the resultant induced polar influence (I) which is transmitted through the linking group $-\text{OCH}_2-$. A similar comparability between the *ortho* directive powers of alkyl and aryl groups has been found in analogous types of ethers of the quinol series (20).

This similarity of action of alkyl and aryl radicals applies, however, only to the consideration of general polarization effects (I) induced by aromatic rings on atoms exterior to them. It is not in accordance with the experimental facts relating to all types of linked ring systems. For example, on comparing compounds of linked ring systems with those containing only one ring system (e.g. X) it has been found that the special activation induced by the alternating polarization mechanism (T) is appreciably less in the case of the compound with the linked ring systems (e.g. IX). This difference arises because there is a distribution between the two rings (A) and (B) of the alternating polarity effect originated by the linking group $(-\text{X}-)$. The tautomeric electron pulses (T), which produce either *ortho-para* or else *meta* substitution as the case may be, are usually considered to occur only in momentarily activated molecules. An activating group (in this case $-\text{X}-$) can be assumed to receive extra (? quantized) energy, or perhaps an extra electron—possibly from an external catalyst or as the result of an intermolecular collision—and to hand on this energy, or electron, very rapidly, by

the tautomeric process, to the actual point at which substitution occurs. One momentary production of an activated grouping in any individual molecule will result in the activation of one point only of potential substitution, and, in the case of a linked ring compound, this may be produced, through the (T) process, in either of the two rings. As the measurable rate of substitution will depend primarily upon the frequency of activation of the directive grouping, and only secondarily upon the course of the tautomeric change subsequently resulting, the chance of resultant activity appearing at any one point of potential substitution in a large conjugated system, such as a molecule with linked aromatic rings, is less than in a more restricted system, such as a molecule containing only one aromatic nucleus. This can best be illustrated by the following reference to experimental fact.

While investigations of the substitution reactions of various methylbenzyl ethers of the catechol and quinol series (see p. 415) showed that the benzyloxy and methoxy groups had comparable directive powers, investigations of the phenyl methyl ether of quinol (XII) showed that substitution occurred exclusively in position 3 in ring (A) (21).

$$CH_3—O—\langle A \rangle—O—\langle B \rangle$$
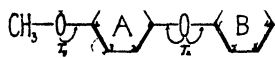
(XII)

The occasional electron pulse activation of the oxygen atom (x), transmitted intermittently to one or other of the two rings is no longer comparable, in ring (A), with the unidirectional activation of the oxygen atom (y) of the methoxy group. This latter group can therefore control the actual mode of substitution in the whole molecule.

There indeed seems to be a tendency for aromatic nuclei to attract to themselves electrons which may be emitted from any adjacent electron source group (22, 23). Support for this view, though drawn mainly from such evidence as the stability of triphenylmethyl and the reactions of conjugated tautomeric systems, is not lacking within the sphere of aromatic substitution. Apart from the case of diphenyl ether, considered above, it is well

illustrated by the inactivity of benzophenone as compared with acetophenone, and of benzoyl derivatives generally in comparison with the corresponding acetyl derivatives. In these cases the difference in activity between similar types of compounds may be expressed through the scheme of Cooper and Ingold (24), according to which decrease in the reactivity of carbonyl compounds corresponds to withdrawal of electrons from the carbon atom of the carbonyl group with consequent increase in the magnitude of the deactivating influence of the $>C=O$ dipole.

As regards its action on any outer substituent group, an aryl radical may be said to diminish the alternating induced polarity of any neighboring group by withdrawing some of the momentary activating electron surges to itself. At the same time it must be regarded as increasing the general reactivity at the more distant parts of the molecule. On the basis of Ingold's classification, the phenyl group is thus to be regarded as of the type $(+I -T)$ when *not* acting as the primary electron source in controlling substitution.

When exerting its inherent directive influence, however, the phenyl group has a most pronounced "electron source" character $(+T)$, for it is a strong *ortho-para* directing group. In the substitution of diphenyl, for example, there is no evidence of the formation of *any* meta derivative, whereas the corresponding system with an alkyl directing group—toluene—may yield as much as four per cent of *meta* derivative on substitution. The negative alternating inductive property of the phenyl group $(-T)$ must therefore be regarded as a secondary effect, originating outside the aromatic nucleus, and not as one of its inherent electronic influences.

This characterization of the essential natures of aromatic polar properties is in full accord with the normal modern conception of aromatic substances being essentially freely mobile tautomeric systems, which yet preserve as a whole one distinct resultant electronic configuration.

More complex linked ring compounds, of the type (XIII), having widely separated aromatic nuclei, in contrast to those

previously considered, show only the normal polar influences of their constituent parts (A), (B), (X), and (Y).
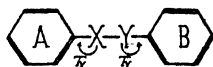
(XIII)

The special interaction of (X) on ring (A) does not affect ring (B), nor does the interaction of (Y) on ring (B) affect ring (A), for electron pulse transmission is rarely possible between the groups (X) and (Y). It is in these compounds therefore that the similarity between the activating properties of alkyl and aryl radicals is most clearly shown, as in the case of the phenyl benzyl ethers to which reference has already been made (p. 415).

Substances containing linking groups such as $-CH=CH-$ or $-N=N-$, which would complete the conjugation between the two aromatic nuclei, have been but little investigated. They undergo ethylenic addition reactions rather than aromatic substitution reactions but, in a case where the latter is possible (azobenzene), the normal independence of action of the two aromatic rings has been observed (17, 28).

With compounds of type (XIII) it is possible to obtain true comparisons of the relative directive properties of the divalent linking groups (X) and (Y), for (X) will activate atoms in ring (A), and (Y) atoms in ring (B) to extents directly proportional to their intrinsic polar powers (T_x and T_y) alone. External influences, such as those due to solvents, will affect both rings equally, though local "solvation" or "electrostriction" effects (25, 26, 27) due to either of the groups (X) or (Y) may be found. For example the well-known effect of concentrated sulfuric acid in rendering an aromatic base an inert, *meta* substituting substance (for which $-N^+: H_3$ has $-I -T$) instead of a reactive, *ortho-para* substituting substance (for which $-NH_2$ has $+I +T$) has been parallelled in linked ring compounds.
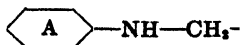
(XIV)

Benzylaniline (XIV) normally substitutes with great ease in ring (A), but its sulfate, in concentrated sulfuric acid solution, nitrates exclusively in ring (B) and yields over 65 per cent of the *meta*-nitro derivative (29). A recent study of the nitration of benzylideneaniline affords another example of the same effect (46). Solvation effects, however, must be regarded as inherent electrochemical properties of these groups, as they arise locally by virtue of the external electrical fields invariably associated with them.

Unfortunately, few comparative data can be deduced from the very slight amount of experimental work which has been carried out with ring systems of type (XIII) up to the present, but, as giving examples of the type of results to be anticipated, the benzoin group of compounds can be briefly considered.

$$\langle A \rangle - \text{CH} - \underset{\underset{\text{O}}{\|}}{\overset{}{\text{C}}} - \langle B \rangle \qquad \langle A \rangle - \text{CH}_2 - \text{CO} - \langle B \rangle$$
$$\overset{|}{\underset{\text{OH}}{}}$$
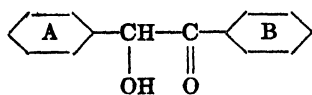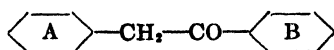
(XV)   (XVI)

In both benzoin (XV) and desoxybenzoin (XVI), the ring (A) is the one first attacked, and reaction occurs in the *ortho* and *para* positions to the neighboring activating $(+I +T)$ linking group (CHOH or CH$_2$). On disubstitution, after the insertion of a deactivating group (e.g., NO$_2$) into ring (A), the other ring (B) may be attacked also, and in it substitution occurs in the *meta* position, subject to the polar influence $(-I -T)$ of the neighboring carbonyl group. Unlike benzil however, benzoin does give some 4,4'- disubstituted product (30) indicating that the general activating influence $(+I)$ of the $-$CHOH$-$ group, adjacent to ring (A), has an actual, though very slight, effect on the more distant ring (B').

No experimental data, unfortunately, are yet available for compounds of type (XIII) in which the linking groups are of comparable directive powers and with which mixed products should be obtained on substitution.

In order to complete the survey of the substitution of linked ring systems, the properties of already substituted linked ring compounds must now be considered in detail.

As has already been stated (p. 412) it is apparent from experimental work that, in any substance of the general type of figure (I) or of figure (XVII), the type of substitution reaction

R—(A)—|XY|—(B)—R
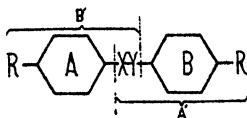
(XVII)

induced in any one ring (A) by any other ring system (A') linked to it is, in every case, constant, no matter what substituent groups (R'), other than linking groups ($-XY-$), may be present in the ring (B) which may affect its own internal substitution reactions. Thus, in the benzophenone series, a substituted benzoyl group ($-CO-C_6H_4R$) *always* has a deactivating ($-I$), *meta* directing ($-T$) influence, whatever the nature of the group ($-R$) (31, 32, 33). Similarly, in the diphenyl ether series a substituted phenoxy group ($-O-C_6H_4R$) always has an activating ($+I$), *ortho-para* directing ($+T$) influence (21, 34, 35, 47).

In the diphenyl series, in which alternate polarity electron pulses could conceivably be transmitted from ring to ring, this constancy of type of substitution product has been demonstrated most conclusively by recent experimental work (11–15). The statement of Vorländer (18) that the substituted benzene ring always preserves its characteristic *ortho-para* directive influence has been firmly upheld, the substituent groups ($-R$) have definitely been shown to have only a secondary influence on the directing effect of one ring on the other, and some investigators have gone so far as to state that any one ring is not at all influenced by modification of the other (11). Though this last sweeping generalization is not absolutely correct (15, 36), there is no doubt that this consistency of *type* of directive action of any ring system has now been proved beyond question. Even in the three isomeric phenylpyridine systems ($C_6H_5-C_5H_4N$), in which the great readiness of the pyridine ring to undergo tautomeric change has specially favored the transmission of alternating polarity effects, this same constancy of type of action is generally

preserved (16), and the same rule seems to apply to other linked aromatic-heterocyclic compounds containing two rings both of aromatic character (18, 37, 38, 48). The very strong *meta* directing influence of the nitrogen atoms acting as "positive poles" within the heterocyclic ring is never greater than the general *ortho-para* directive influence of the whole ring system.

This is exactly what one would anticipate on the basis of the modern conception of the nature of the alternating polar influence, for even a very occasional activating electron pulse $(+T)$, that could cause a molecule to react, is bound to predominate over any deactivating effect $(-T)$ which would not result in the occurrence of substitution.

The accumulation of deactivating influences $(-I)$ in a completely conjugated radical may however, by attracting away electrons, bring about the obliteration of electron expelling $(+T)$ tautomeric changes, or rather, may cause them to be reversed in direction. As an instance of this, it has been shown that 2-phenylglyoxaline-4,5-dicarboxylic acid nitrates mainly in the *meta* position in the benzene ring, while the unsubstituted phenylglyoxalines nitrate mainly in the *ortho* and *para* positions in the benzene ring (39).

The fact that, for any compound of type (XVII), the position of attack in ring (B) is independent of the *position* of the substituent group $(-R)$ in ring (A) again might be deduced from the electron pulse conception of directive action, though not from all of the earlier theories of alternating polarity.

Once an activating electromeric change brings about the introduction of a new electron into an aromatic ring, then *ortho* or *para* substitution must result, no matter where the original electron source may have been situated in the directing group. Similarly, any abstraction of electrons from an aromatic ring to an outer "electron sink" must render impossible attack by an electropositive substituting ion in these same positions (8, 9). It is the direction of the electronic movement and not its origin which can be correlated with the subsequent substitution reaction.

However, the more important experimental fact that, in addition, the polar nature of the group $(-R)$ (whether an "electron

source" like $-OH$, or an "electron sink" like $-NO_2$) is unable to alter the type of directive action of ring (A) can only be explained through inferring that the alternating polar influence (T) cannot be transmitted from ring to ring. Here, on general considerations, it would have been anticipated that internuclear electron transmission might have been possible in certain cases, particularly in fully conjugated compounds such as diphenyl, stilbene or azobenzene derivatives.

Both aromatic ring systems, with mobile electrons which of their own induce "electron source polarization" $(+T)$, and the linking groups, which are not usually potential electromeric systems, must act as almost complete bars to the transmission of those electron pulses which are so very powerful within a single aromatic nucleus. One may suggest that this inability of an aromatic ring to transmit an electromeric polarizing influence to another ring is possibly due to its tendency to attract to itself, and to retain, extra electrons (22, 23). See p. 417.

More detailed examination of substitution reactions in linked ring systems, however, reveals the equally important fact that, though the general type of directive influence of any ring system is preserved unchanged on substitution, the magnitude of this directive effect is distinctly affected by the presence of the substituent group.
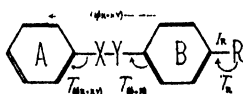
(XVIII)

Therefore, though the alternate electron pulse activation (T_R) (figure XVIII) of the group $(-R)$ in the ring (B) is unable to reach ring (A), the general electron drift influence (I_R) can be transmitted through the linking group $(-XY-)$, in spite of the fact that, in most cases, the linking group exerts a damping effect upon the electron transmission, seriously diminishing its resultant intensity. This experimentally demonstrated conclusion illustrates perhaps the clearest of all the distinctions between the

intrinsic natures of the general inductive (I) and the alternating tautomeric (T) induced polarization influences.

The transmission of the general electronic drift influence of a group ($-R$) to a distant ring has been demonstrated most clearly in the diphenyl ring system, in which there is no linking group that might reduce the magnitude of the resultant induced electrical potential. Many experiments have shown that the inhibiting electron drift ($-I$) due to the presence of a nitro group, and to a less extent also due to the presence of a halogen atom, exerts its influence throughout the whole of the complex system by decreasing generally the rate of chemical reaction in both rings (12–15). It is the action of this general polar influence that results in the unsymmetrical substitution of diphenyl derivatives that has been the subject of so much experimental investigation since the year 1912 (1, 14, 15). It has been shown, for example, that though a chlorophenyl (ClC_6H_4-) or a bromophenyl (BrC_6H_4-) group has a more powerful directive influence than the corresponding halogen atom, yet the introduction of a nitro group into either renders the substituted aromatic ring ($HalC_6H_3NO_2-$) less strongly directing than the halogen atom, on account of the inhibiting electronic drift ($-I_{NO_2}$) initiated by the presence of the nitro group (40, 15, 49) (figure XIX).

(XIX)
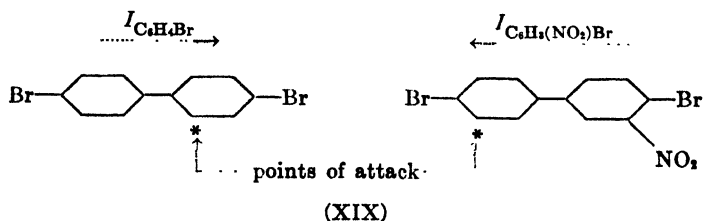
A similar explanation (41, 11) has been given for the formation of the isomeric dinitrobenzidines and dinitrotolidines of Cain (1), which were originally thought to have been stereoisomers and not structurally different compounds. Similar effects have also been observed in the diphenyl ether, phenyl benzoate and phenylbenzene sulfonate series (34, 50). For example 2,4-dichloro-2',4'-dinitrodiphenyl ether nitrates in position 5 in ring (A) (figure XX) and not in position 6 as would otherwise be anticipated.

(XX)
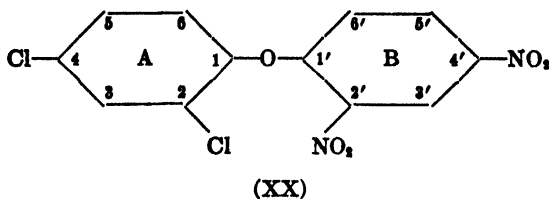
Further proofs, of more convincing nature, of the existence of this internuclear transmission of the general polarizing influence (I) have been given in several recent quantitative researches of Robinson and his colleagues. For example, in continuation of the investigations on the relative directive powers of the groups present in benzylguaiacol, to which reference has already been made (see p. 415), Oxford and Robinson have shown that while the directive power of the benzyloxy group towards its *para* position has a magnitude of 113, relative to that of the methoxy group as 100, the nitrobenzyloxy group has a relative directive power of magnitude only 67, and the chlorobenzyloxy group one of only 82 (42). In both cases the magnitude of this general polar effect is practically independent of the position of the substituent group (NO₂ or Cl) within the directing benzyloxy group. The same effect has also been found among substituted benzamide derivatives (43), and the results may be indicated diagrammatically as in figure (XXI).

(XXI)
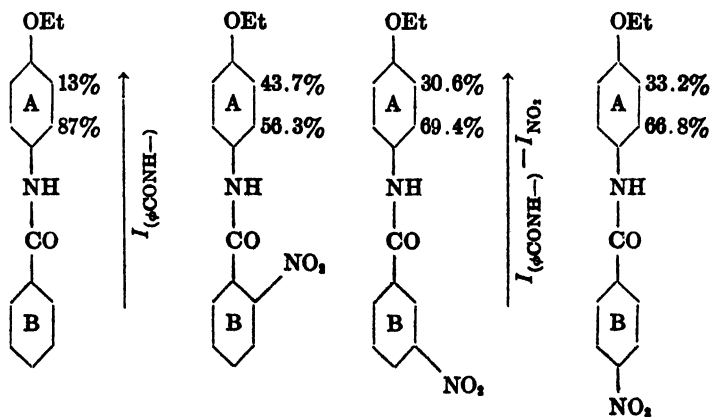
Thus even such a complex and highly polar linking as the $-NH-CO-$ group is unable to block completely the transmission to ring (A) of the electron drift induced by the nitro grouping in ring (B). The experimental results show too that the electron pulse effect (T) of the nitro group is scarcely noticed in ring (A), as the resultant activity in that ring due to the substituted benzamido group is practically independent of the position of the nitro group in ring (B).

That linking groups exert a damping effect upon the transmission of general induced polar effects from ring to ring, however, may be seen from the examination of many substitution results. For example, the very powerful activating groups $-OH$ and $-NH_2$ are unable to induce any appreciable reactivity in the more distant ring in derivatives of both the benzophenone and the azobenzene series (17, 31, 33), though the linking groups concerned ($-CO-$ and $-N{=}N-$) differ very markedly from each other with respect to their own polar influences.

These "damping effects" of the linking groupings may be traced to two distinct sources. Firstly, the linking group, merely by separating the two rings, increases the distance over which the polar influence must be exerted, and so diminishes the magnitude of the resultant induced electrical potential. Secondly, most linking groups contain atoms of polar character which both act as "electron shields" to the original induced electrical potential, and also induce new electronic drifts on their own account, frequently far more potent in magnitude. The importance of the distance factor in hindering the transmission of electronic drifts may be gauged by comparing the substitution results in the diphenyl series with those in the diphenylmethane and diphenylethane series. In the diphenyl series the substituent groups in one ring are occasionally powerful enough to induce unsymmetrical substitution (see p. 424), but in the diphenylmethane and diphenylethane series no such effects have yet been observed, although similar types of compounds have been investigated (44).

The polar action of the linking group, however, contributes most to the prevention of electronic drifts through long chains

of atoms. For example, in all qualitative experiments, the benzophenone system, containing a strong partial dipole group $(\overset{+}{C}=\overset{-}{O})$ between the two rings, seems to react as if it contained two completely independent aromatic rings, both subjected only to the polar influences of the linking group and of such other substituents as they may contain. As in the closely corresponding benzoin series however (30), accurate quantitative research may reveal the existence of a .very slight residual effect. Benzanilide, for example, should contain a still more effective damping linking group (*viz.*, $-NH-CO-$), yet, as has been mentioned, quite an appreciable amount of induced electrical polarity may be transmitted from ring to ring.

This characteristic decrease in intensity of both the polar influences owing to increasing distance of action, and to the intervention of intermediate groupings, is well illustrated by considering the series of compounds nitrobenzene (XXII), ω-nitrostyrene (XXIII) and nitrodiphenyl (XXIV), with which may also be exemplified the stages in the transition, in properties as well as in structure, from a simple aromatic compound to a linked aromatic ring compound.

(XXII)   (XXIII)   (XXIV)
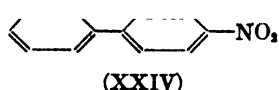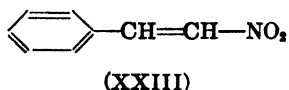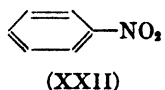
Nitrobenzene is a kationoid system $(-I-T)$, predominantly deactivating and *meta* substituting, whereas nitrodiphenyl—a benzenoid system—is much more reactive and is completely *ortho-para* substituting $(+T)$. Even in the intermediate compound (XXIII) the presence of the linking $-CH=CH-$ group serves to reduce the tautomeric $(-T)$ effect of the nitro group to a second order influence, far weaker than that of the nearer activating $(+T)$ double bond (10).

In conclusion it may be stated that the study of linked ring systems shows most clearly the inherent properties and the distinctions between the general electron drift and the alternating tautomeric electron pulse effects, both of which can occur in aromatic compounds. The first influence (I), constant in action and

electrostatic in character, can be transmitted over relatively great distances. It can act possibly through free space, and certainly through any intervening grouping. The second influence (T), of electrodynamic character, is temporarily very powerful indeed, but is essentially sporadic and variable in action. It can be transmitted only within readily mobile, completely conjugated, tautomeric systems. Even in these systems too, slight intermediate effects, originating in intervening atoms, may easily divert the path of the activating electromeric energy transmission or may modify its resultant intensity at any particular point within a molecule.

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THE CRYSTAL STRUCTURES OF ORGANIC COMPOUNDS[1]

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Methods for the analysis of crystal structures of inorganic compounds have been greatly extended since M. von Laue's prediction of x-ray diffraction by crystalline lattices. Within recent years generalizations based upon physical laws and upon empirical analyses of existing structural information, together with increase in knowledge concerning the factors affecting the intensities of x-ray reflections from crystals, have made possible determinations of the structure of very complex compounds having low crystallographic symmetries. The concept of inorganic compounds as composed of spatial arrays of approximately spherical atoms of "constant radii" in contact (1) has, in a somewhat modified form, proven of great utility in structure determinations (2, 3, 4).

Complete determinations of structure have been made for but few organic compounds. The results obtained have not markedly facilitated the analysis of other structures. The difficulties of analysis partially arise from the low crystallographic symmetries of most organic crystals. The factors determining the intensities of the x-radiation coherently scattered from atoms of low atomic number, such as oxygen, nitrogen, carbon, and hydrogen, are not as completely evaluated as for heavier atoms. Thus such atoms can not easily be allocated in the structures, and in the case of hydrogen atoms the data as to the intensity of reflection alone are insufficient to permit their allocation.

[1] To economize space no exposition of the notation employed for crystal structures is included in this review. Reference 6a cites a complete discussion of notation and technical terms.

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Completely determined atomic arrangements for some organic compounds indicate that there are groups of atoms in such crystals that are repeated as groups throughout the crystals. The groups that are to be identified as the organic molecules are probably to be characterized by the approximate constancy of distances of closest approach between adjacent atoms within the groups. It should be possible to determine from the derived crystal structures alone the characteristic carbon to nitrogen, carbon to carbon, etc., distances in molecules of organic compounds in the solid state, and to check the constancy of the distances. The spatial distributions of the molecules and their distances of approach to other molecules have not yet been shown to be similar in different compounds. Since the intensities of the x-ray beams diffracted from the crystals are functions of both the intramolecular and the intermolecular configurations, this apparent lack of regularity increases most markedly the difficulties of the structure analyses.

Information obtained from the x-ray diffraction patterns of some organic crystals is described in this paper. Results of particular significance to structural organic chemistry are discussed under the specific compounds. An attempt is made to obtain from the structures discussed certain relationships which might be of assistance in structural analysis. No effort is made to give an exhaustive survey of all available x-ray diffraction data from organic compounds, since the greater part of these data merely serve to extend the crystallographic descriptions. Such information is summarized in standard references (5) and is currently abstracted in the Zeitschrift fur Kristallographie.

TYPES OF INFORMATION OBTAINED

The analysis of the x-ray diffraction data from a particular compound leads to a determination of the smallest parallelopiped which, when repeated, gives the macroscopic crystal. This is the "unit of structure." It must contain an integral number of molecules or formula weights of the substance.

The characteristic types of reflections observed to be absent, together, if necessary, with a crystallographic determination of

the crystal class, determine the symmetry elements of the unit of structure and thus lead to one of the 230 groups of operations giving crystalline symmetry. This is the space-group.

The observation that the number of molecules in the unit of structure is less than the number of asymmetrical points obtained by repeating a point according to the symmetry operations of the space-group requires the molecule to have symmetry. This, with certain exceptions noted later, gives the minimum possible symmetry of the molecule. The actual symmetry may be, and sometimes is, greater than this minimum. If the number of molecules in the unit of structure is greater than the number of asymmetrical points, then the molecular groups must be either crystallographically non-equivalent or associated in groups that are crystallographically (6) equivalent. The structures of the aromatic hydrocarbons which are discussed later illustrate these requirements.

It is sometimes possible to determine completely the position of each constituent atom without the use of assumptions concerning the probable arrangement. Such complete structure determinations have supplied information of fundamental importance to structural organic chemistry. The complexity of the problem, however, usually necessitates the reverse procedure of assuming structures which are chemically logical and ascertaining whether they can or cannot explain the observed intensities of reflections.

In the following partial review complete structure determinations are first considered. The structures, if they are sufficiently complete, are described by giving the atomic positions in terms of coördinates referred to specified axes (6a). Some results of determinations of the unit of structure, of the space-group and of molecular symmetry are discussed. Atomic positions are represented by small circles on the figures; these circles do not indicate the relative atomic sizes. The distances on the figures are given in Ångström units (1 Å. = 10^{-8} cms.).

STRUCTURE DETERMINATIONS

The crystal structures of halogen substituted compounds

The amplitudes of the waves coherently scattered by various kinds of atoms in a crystal are, in the first approximation, func-

tions of the atomic number and of sin θ/λ, where θ is the angle of reflection and λ the wave length of the x-radiation. It is usually assumed that at 0° the amplitude of the scattered wave is directly proportional to the atomic number. In a crystal containing atoms of high and low atomic number the intensities of reflection
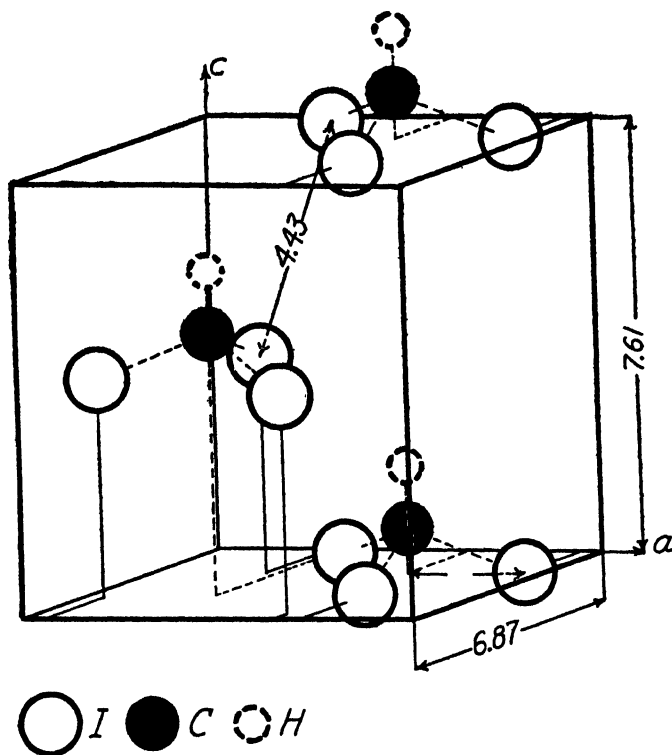
FIG. 1a. IODOFORM, CHI$_3$. THE UNIT OF STRUCTURE

The indicated positions of the hydrogen atoms are hypothetical.

of x-radiation depend most markedly upon the distributions of atoms of high atomic number. In a crystal containing, for instance, carbon, hydrogen, and iodine, the effect of the carbon and hydrogen on the intensities of reflection often can not be detected. For this reason it is sometimes possible to determine quite accurately the positions of the heavier atoms in crystals

having complex structures.   Advantage has been taken of this fact in the structure analyses of a number of aliphatic compounds discussed below.

Iodoform (7).   The hexagonal unit of structure containing
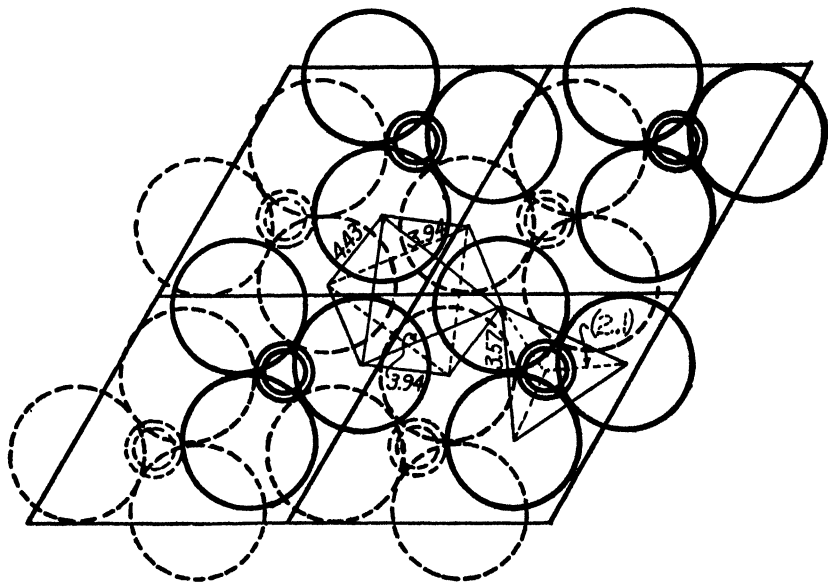
FIG. 1b. IODOFORM, CHI₃.   A PROJECTION ON THE BASAL PLANE (00.1)

The octahedral arrangements of atoms of separate molecules are shown on the projection.   Iodine atoms below the plane of projection are shown as large dotted circles; the carbon and hydrogen atoms are shown as small dotted circles.

$2CHI_3$ has c = 7.61 Å. and a = 6.87 Å.   The iodine atoms are at space-group C_6^6 (6a)

$$x, y, z; y - x, \bar{x}, z; \bar{y}, x - y, z$$

$$\bar{x}, \bar{y}, z + \tfrac{1}{2}; x - y, x, z + \tfrac{1}{2}; y, y - x, z + \tfrac{1}{2}$$

with x = 0.346 − 0.362, and y = 0.038 − 0.056.   (Limits of certainty are given; z may be assumed to be zero.)   The minimum molecular symmetry is probably a threefold axis.   The unit of structure and a projection on (00.1) are shown in figures 1a and 1b.

The relative positions of the iodine atoms are defined by two

determined parameters.   The interatomic distances are shown in figures 1 and 2.   If the carbon atoms are at $\frac{1}{3}$, $\frac{2}{3}$, u; $\frac{2}{3}$, $\frac{1}{3}$, $u + \frac{1}{2}$ (u_C is undetermined), then the minimum I—I distance, about 3.57 Å., is that between atoms of the same molecule.   In this case the iodine atoms of separate molecules are located at the corners of octahedra the edges of which are 3.94 Å. and 4.43 Å. in length (note figure 1).

A representation of a single molecule is shown in figure 2.   In this figure the dotted portions are unknown.   It is possible, but quite improbable, that the carbon atoms are at $00u$; 00, $u + \frac{1}{2}$ (space-group C_{6v}^3).   In either this or the above case the C—I distance is > 1.97 Å., and is probably about 2.10 Å.
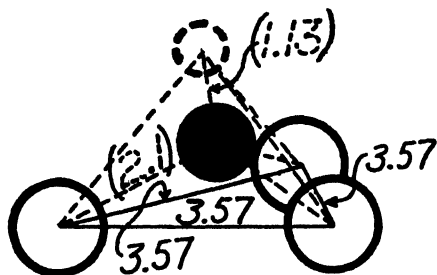
Fig. 2. Iodoform, CHI_3. Molecular Configuration

The undetermined portions are dotted.   See figure 1b for description.

1,2,3,4,5,6-Hexabromo- and hexachloro-cyclohexane (8).   The cubic units of structure containing $4C_6H_6X_6$ have the dimensions $a = 10.49$ Å. ($C_6H_6Br_6$) and $a = 10.07$ Å. ($C_6H_6Cl_6$).   The halogen atoms are in the general positions of the space-group T_h^6.   The peculiarities in the intensities of reflection from (111) in various orders made possible determinations of the three parameters defining the positions of the halogen atoms.   The parameter values are: $x = 0.39$, $y = 0.22$, and $z = 0.085$ for both $C_6H_6Br_6$ and $C_6H_6Cl_6$.

The minimum molecular symmetry is a threefold axis and a center of symmetry.   The molecular centers are at

(a) $0, 0, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$; $0, \frac{1}{2}, \frac{1}{2}$

or

(b) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, 0, 0; 0, \frac{1}{4}, 0; 0, 0, \frac{1}{4}$

These two possible molecular configurations are shown in figure 3. It is quite probable that the correct structure is as shown in figure 3a and that figure 3b represents the closest approach of halogen atoms of separate molecules (3.74 Å.). Here, as for CHI₃ (compare);* the halogen atoms of separate molecules are approximately at the corners of an octahedron (figure 3b).
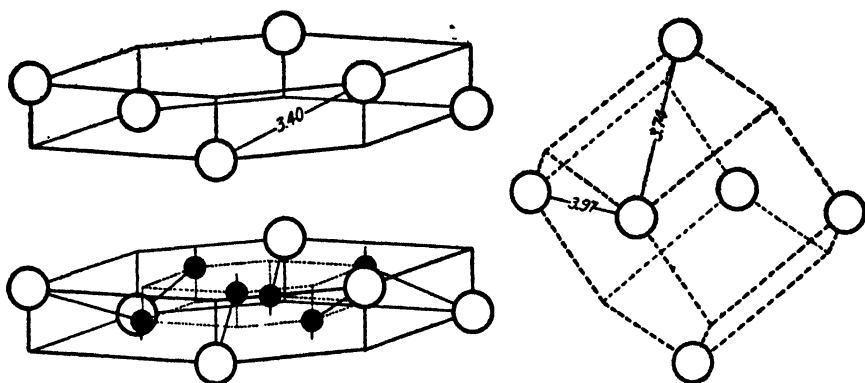
Fig. 3a. 1,2,3,4,5,6-HEXABROMOCYCLOHEXANE,   C₆H₆Br₆. MOLECULAR CONFIGURATION

Possible positions of the carbon atoms (black circles) are indicated.

Fig. 3b. 1,2,3,4,5,6-HEXABROMOCYCLOHEXANE,   C₆H₆Br₆. OCTAHEDRAL ARRANGEMENT OF ATOMS OF SEPARATE MOLECULES

Bromine atoms alone are shown.

If the carbon atoms are assumed to be situated as shown in figure 3a, the C—C distance being 1.54 Å. as in the diamond, with $x = -0.076$, $y = +0.099$, and $z = -0.065$ for the bromide, and $x = -0.079$, $y = +0.103$, and $z = -0.068$ for the chloride, then the C—Br distance is about 1.94 Å., and the C—Cl distance is about 1.81 Å. This assumed structure gives a tetrahedral distribution of the carbon valences, which might be expected from the aliphatic nature of the compound.

Some simple derivatives of ethane (*9*). The results obtained from x-ray examinations of a number of orthorhombic derivatives of ethane are partially shown in table 1.

The dimensions of the orthorhombic unit of structure containing $4C_2X_aY_{6-a}$ are given in table 1. The space-group is V_h^{16} and the positions of the halogen atoms are defined by ten parameters. A molecule possesses a plane of symmetry and it is probable that two of the halogen atoms are in this plane and four are outside it as a plane of symmetry. The probable distances (r) of the halogen atoms from this plane are given in the fifth column of table 1, and a halogen to halogen distance ($2r$) in the last column.

TABLE 1

A summary of the results obtained from some simple derivatives of ethane

COMPOUND	a IN Å.	b IN Å.	c IN Å.	r IN Å.	$2r$
C_2Cl_6............................	11.51	10.14	6.39	1 45 ±0.04	2.90
C_2Br_6............................	12.07	10.70	6.72	1.58 ±0.04	3.16
$C_2Cl_4Br_2$......................	11.73	10.37	6.50	1.55 ±0.04	3.10
	11.61	10.35	6.31	1.55 ±0.04	3.10
C_2Br_5F.........................	11.84	10 75	6.56	1.58 ±0.03	3.16
$C_2Cl_2Br_4$......................	11.77	10.44	6 54	1.52 ±0.09	3.04
$CH_2CBr_2 \cdot CBr_2CH_2$...........	11.70	10 90	6 55	1.59 ±0.05	3.18
	11.70	10.44	6.57	1.78 ±0.01	3.56

The observed quartering of planes ($hk0$) (for C_2Cl_6 and C_2Br_6) for which h is odd and halving of planes ($hk0$) for which h is a multiple of four require the parameters of the halogen atoms in the a direction to be $\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$, or $\frac{7}{8}$. The observed presence of planes ($h0l$) for C_2Cl_6 and C_2Br_6 with h odd prohibits a molecule from having a second plane of symmetry, parallel to (100), and suggests instead that it has an approximate center of symmetry. If this is true, then the shortest Br—Br distance in C_2Br_6 between bromine atoms on different carbon atoms would probably be about 3.40 Å., in contrast with about 3.16 Å. on the same carbon atom. This second distance is somewhat less than the x-x separation in $C_6H_6Br_6$, but the distances, nevertheless, are closely similar. The halogen atoms of one molecule are at the corners of an octahedron (see figure 4).

The structure analyses were not carried further, but if one assumes that the carbon atoms are in the plane of symmetry, as seems highly probable, that their separation is about 1.54 Å., that the bromine or chlorine atoms in the plane of symmetry are a distance $2r$ from those outside that plane, and that the carbon atoms are equidistant from the halogen atoms attached to one carbon atom, then a molecule of the type shown in figure 4 is obtained. In such a molecule the halogen-carbon distances, not assumed, are for Br—C, 1.97 Å., for Cl—C, 1.81 Å., in agreement with the values found on the basis of certain assumptions
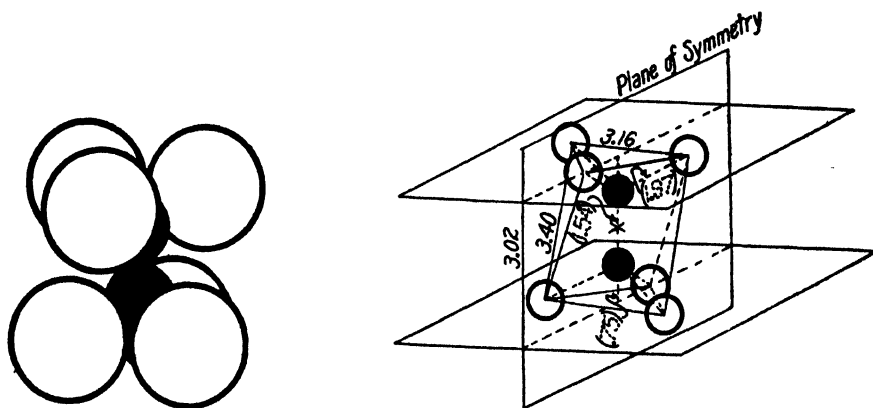
FIG. 4. HEXABROMOETHANE, C_2Br_6. A POSSIBLE MOLECULAR CONFIGURATION

The pseudo center of symmetry is indicated by the cross mark. The carbon atoms are represented by black circles, the halogen atoms by open circles.

for $C_6H_6Br_6$ and $C_6H_6Cl_6$. The parameters in the c direction have not been determined, so it is impossible to allocate the molecules in the structure.

In the case of the last four compounds given in table 4 the plane of symmetry is present (requiring for instance the F atom of C_2Br_5F to be on the plane of symmetry) but the peculiarities of reflections from ($hk0$) are absent, so that their structures, although closely similar to those of C_2Cl_6 and C_2Br_6, can not be as thoroughly determined.

The two modifications of $C_2Cl_4Br_2$ have in the past been assumed to be $CCl_2Br \cdot CCl_2Br$, and $CCl_3 \cdot CClBr_2$. The intensity measurements for the two compounds, however, show none of the differences which would be expected if the first of these formulas is correct. The analysis of the results rather suggests that both crystalline modifications have the formula $CCl_3 \cdot CClBr_2$. It is difficult on this basis to see why crystallization from particular solvents should not result in changing one modification into the other.

Observations were also made on tetragonal modifications of $CH_3 \cdot CBr_2 \cdot CBr_2 \cdot CH_3$ and $C_2(CH_3)_4Br_2$ and on the orthorhombic $(CH_3)_3C \cdot C(CH_3)_2OH$, but the structures were more complex in these cases; the analyses were not as complete as for the orthorhombic crystals described above.

Other halogen compounds. Iodosuccinimide (10), *m*-iodobenzoic acid (11), carbon tetraiodide (12), carbon tetrabromide (12), hexachloro- and hexabromo-benzene (12), tetrachloronaphthalene (13, 14), and 1,2,3,4,5,8-hexachloronaphthalene-1,2,3,4-tetrahydride (14).

Observations have been made on the above compounds, but the positions of the halogen atoms have not been determined, although this could perhaps readily be done in some of the cases if sufficient experimental data were available. In particular the observations on CI_4 and CBr_4 (12) may be insufficient, since similar results obtained from the analogous SnI_4 have been shown to be seriously in error (15).

The determined units of structure of hexabromobenzene and hexachlorobenzene are shown in table 5. It is to be noted that the length of the b axis (the symmetry axis) is 3.84 Å. for the chloro derivative and 4.04 Å. for the bromo derivative. These values are but slightly greater than the halogen to halogen distances of separate molecules previously noted in aliphatic compounds. It suggests that the length of the b axis is determined by the closest distance of approach between carbon and halogen atoms of separate units of structure.

Observations on vapors

Interference has been noted in x-radiation and in high velocity electron beams, scattered from vapors of organic compounds containing chlorine. The interference maxima are determined by the intramolecular relationships. Results obtained from CCl_4 (16, 17) indicate that the Cl—Cl distance within the molecule, assuming a regular tetrahedral configuration, is 3.3 Å. (16), or 3.14 Å. (17); the corresponding C—Cl distance is 2.02 Å. or 1.91 Å.

TABLE 2

Halogen to halogen distances in some organic compounds

DISTANCE	COMPOUND	SEPARATION			REMARKS
		On same carbon atom	On adjacent carbon atoms	On separate molecules	
I—I.............	CHI₃	3.57	—	3.94	
Br—Br.........	C₆H₅Br₆	—	3.40	3.74	
Br—Br.........	C₂Br₆	3.16	3.40	—	
Br—Br.........	C₆Br₆	—	—	4.04	Questionable
Cl—Cl.........	C₆H₆Cl₆	—	3.26	3.59	
Cl—Cl.........	C₂Cl₆	2.90	3.33	—	
Cl—Cl.........	C₆Cl₆	—	—	3.84	Questionable
Cl—Cl.........	C₂H₂Cl₂ *cis*	—	3.6	—	Gas
Cl—Cl.........	CCl₄	3.30	—	—	Gas
		3.15	—	—	
Cl—Cl.........	C₂H₄Cl₂ (1, 1)	3.40	—	—	Gas
Cl—Cl.........	C₂H₄Cl₂ (1, 2)	—	4.4	—	Gas
Cl—Cl.........	C₂H₂Cl₂ *trans*	—	4.1	—	Gas

These values agree within the limits of experimental error with those obtained from C_2Cl_6 and $C_6H_6Cl_6$.

Observations of x-radiation scattered by *cis*- and *trans*-1,2-dichloroethylene and by 1,1- and 1,2-dichloroethane (18) indicate that in these compounds the Cl—Cl distances are:

$$a_{cis} = 3.6 \text{ Å}. \qquad a_{trans} = 4.1 \text{ Å}.$$

$$a_{1,1} = 3.4 \text{ Å}. \qquad a_{1,2} = 4.4 \text{ Å}.$$

These distances are compared in table 2 with those obtained from crystal structure determinations.

The values obtained for the Cl—Cl distances in 1,2-dichloro-ethane and *trans*-1,2-dichloroethylene are probably not to be compared with the values found for 1,2,3,4,5,6-hexabromocy-clohexane and hexabromoethane, since these latter correspond to other than minimum distances of separations. The structural formulas are probably:

cis-1,2-Dichloroethylene   *trans*-1,2-Dichloroethylene

1,1-Dichloroethane   1,2-Dichloroethane
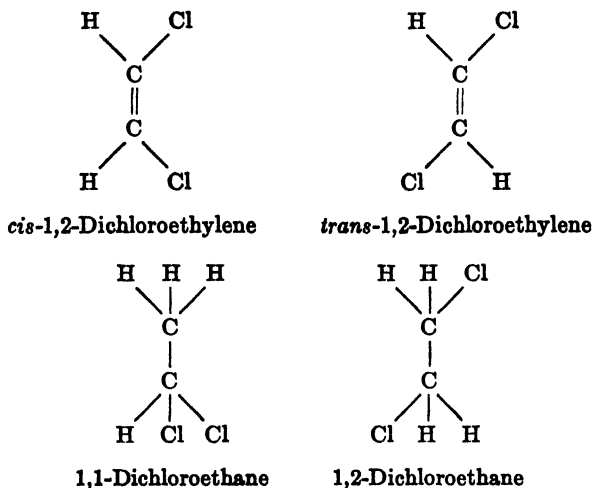
The particular formula of 1,2-dichloroethane is required by the rather large chlorine to chlorine distance in that compound (table 2).

The results obtained from the limited number of aliphatic halogen compounds examined indicate that the halogen-carbon distances are approximately constant in such substances. The values determined from various compounds are listed in table 6.

It is known from theories of organic chemistry that the halogen atoms of the compounds listed in table 2 are not united to one another by "primary" valence forces. The interatomic distances, since they are much greater than those required by probable atomic diameters, are in agreement with this concept. There is, however, a greater constancy in the halogen-halogen distances listed in table 2 than would perhaps be required by the constraints of characteristic carbon-halogen distances. The persistent regularity in the relative positions of the halogen atoms of

separate molecules also suggests that interaction of halogen atoms plays a prominent rôle in both the intermolecular and the intramolecular relationships.

Structure determinations for carbon and some carbon compounds

The high crystallographic symmetry of a few organic compounds has facilitated their complete structure determinations. In one case the analysis was markedly aided by selecting a compound which contains only one molecule in the unit of structure, thus avoiding the difficulty produced by the intermolecular relationships. Examinations of. the members of homologous series, although complete structure determinations could not be made, have nevertheless yielded much information.

In the following discussion the possible positions of the hydrogen atoms will not be considered, save in the case of hexamethylenetetramine. It is probable that these atoms play some rôle in determining the intermolecular relationships. One can assume that the C—H distance is about 1.13 Å., and the N—H distance about 1.08 Å., corresponding to the values found from analysis of band spectra of CH and NH (19).

Diamond (20), graphite (21, 22). The crystal structures of the two crystalline modifications of carbon are shown in figure 5.

In the diamond, which has a cubic structure, each carbon atom is surrounded by four other carbon atoms placed at the corners of a regular tetrahedron. This supports the original van't Hoff hypothesis of the tetrahedral arrangement of the carbon valencies. This arrangement was early introduced as a prototype for the crystal structures of aliphatic compounds. The observed C—C distance in the diamond is 1.54 Å. This distance has been introduced as a basic assumption in some structure determinations.

In graphite, the hexagonal modification of carbon, the carbon atoms in one plane are associated as an interlocked group of hexagons. The closest distances of approach of carbon atoms in this plane are 1.42 Å., while carbon atoms in separate planes are at least 3.40 Å. apart. A flat hexagonal configuration is similar to the formula usually assigned to benzene. For this reason it
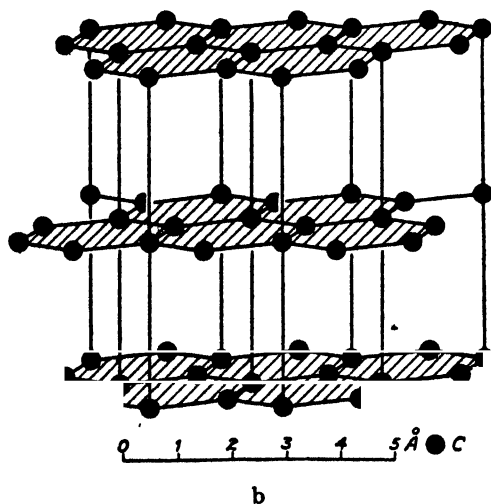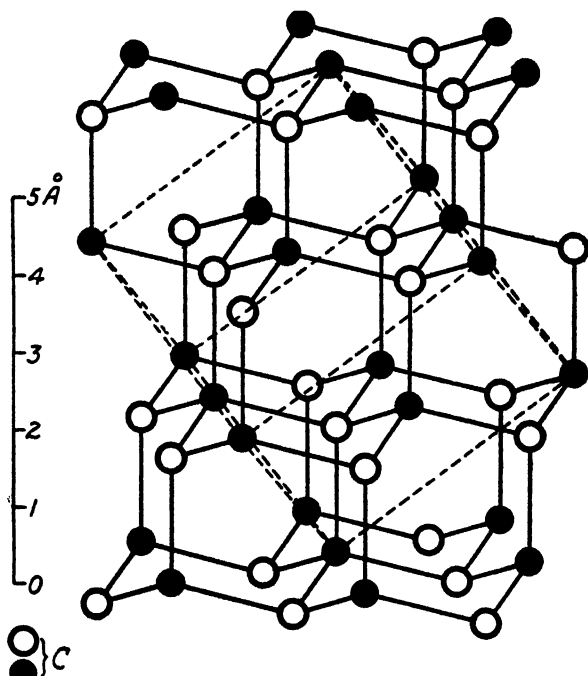
FIG. 5a. DIAMOND, C. 5b. GRAPHITE, C. ATOMIC ARRANGEMENTS IN THE TWO
CRYSTALLINE MODIFICATIONS OF CARBON
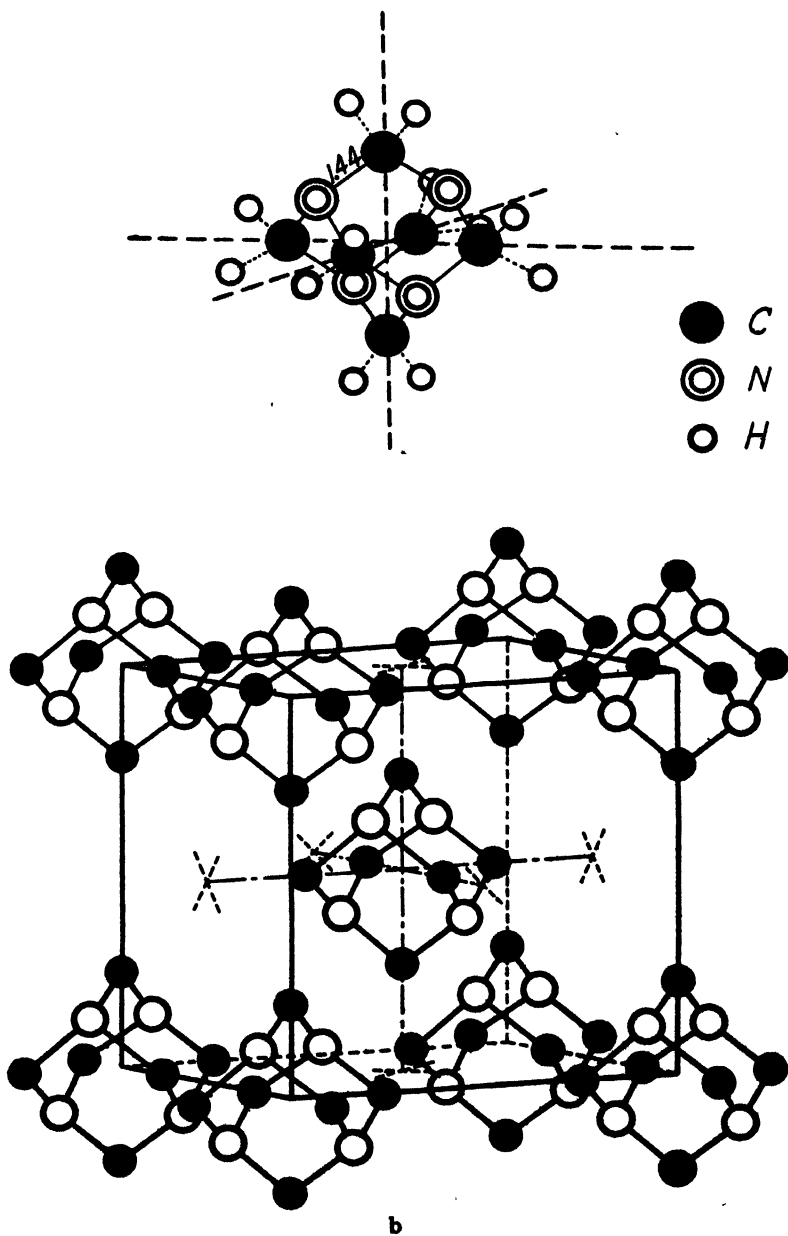
FIG. 6. HEXAMETHYLENETETRAMINE, $C_6H_{12}N_4$. THE UNIT OF STRUCTURE AND THE MOLECULAR CONFIGURATION

Possible positions of the hydrogen atoms are indicated.

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was expected that the crystal structures of benzene derivatives might be more closely related to that of graphite than to that of diamond. Hexagonal groups of atoms are also present in the diamond structure, but the atoms of these groups are not coplanar. In the diamond each carbon atom is surrounded most closely by four other carbon atoms, rather than by three other carbon atoms as is the case for graphite. Similarities are to be noted between the structures of hexamethylbenzene and graphite.

Hexamethylenetetramine (23). The body-centered cubic unit of structure containing $2C_6H_{12}N_4$ has $a_0 = 7.02$ Å. The analysis was facilitated by assuming the existence of $C_6H_{12}N_4$ molecules. The determined atomic positions are:

C at $u00$; $0u0$; $00u$; $\bar{u}00$; $0\bar{u}0$; $00\bar{u}$

$\frac{1}{2}+u, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}+u, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}+u; \frac{1}{2}-u, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}-u, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}-u$

N at vvv ; $v\bar{v}\bar{v}$; $\bar{v}v\bar{v}$; $\bar{v}\bar{v}v$

$\frac{1}{2}+v, \frac{1}{2}+v, \frac{1}{2}+v; \frac{1}{2}+v, \frac{1}{2}-v, \frac{1}{2}-v; \frac{1}{2}-v, \frac{1}{2}+v, \frac{1}{2}-v; \frac{1}{2}-v, \frac{1}{2}-v, \frac{1}{2}+v$

with $u = .235$ and $v = 0.12$.

The unit of structure and the molecular configuration, with possible positions of the hydrogen atoms, are shown in figure 6. The minimum molecular symmetry is that of the point group T or T_d. Each carbon atom is surrounded by four atoms at least two of which, nitrogen atoms, are approximately at the vertices of a regular tetrahedron. Each nitrogen atom is equidistant from three carbon atoms, but is not in the plane of the carbon atoms. The minimum N—C distance is about 1.44 Å. The minimum distance between the C atom of a (CH_2) group of one molecule and that of another is about 3.72 Å.

Urea (24), thiourea (24, 25), acetamide (26). Both urea and hexamethylenetetramine are monoacidic bases and form addition compounds with salts and with molecular compounds. The crystal structures of these substances might be expected to give some indication of these heteropolar characteristics.

The tetragonal unit of structure contains $2CO(NH_2)_2$ (see figure 7a) and has $a = b = 5.73$ Å., $c = 4.77$ Å. The atomic positions are:

$$O \text{ and } C \text{ at } 0\tfrac{1}{2}v; \tfrac{1}{2}0\bar{v}$$

$$N \text{ at } u, \tfrac{1}{2} - u, v; \tfrac{1}{2} - u, \bar{u}, \bar{v}; \bar{u}, u + \tfrac{1}{2}, v; u + \tfrac{1}{2}, u, \bar{v}$$

with $u_N = .13 \pm .01$, $v_N = .20 \pm .02$, $v_C = .32 \pm .02$, and $v_O = .57 \pm .03$.
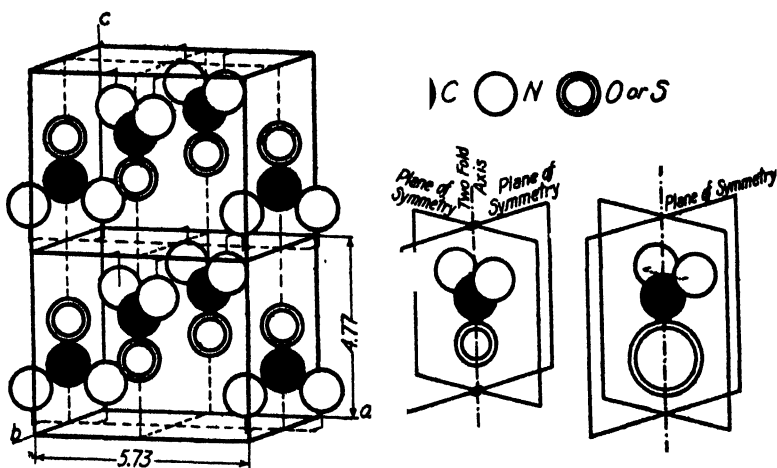
FIG. 7a. UREA, $CO(NH_2)_2$. THE ATOMIC ARRANGEMENT

FIG. 7b. UREA, $CO(NH_2)_2$, AND THIOUREA, $CS(NH_2)_2$. THE MOLECULAR CONFIGURATIONS AND MINIMUM MOLECULAR SYMMETRIES

The urea molecule is required to have two planes of symmetry and a twofold axis of symmetry (figure 7b). The interatomic distances within a urea molecule are C—O, 1.05 − 1.42 (about 1.30); C—NH$_2$, 1.07 to 1.30 (about 1.20). The NH$_2$ groups of one molecule are most closely surrounded by the oxygen ends of other molecules (figure 7a), as might be expected from the heteropolar nature of the compound. The minimum distance between an O atom and an NH$_2$ group of separate molecules is about 3.15 Å.

In the crystalline state the formula must be a symmetrical one,

$$O=C \begin{smallmatrix} NH_2 \\ \\ NH_2 \end{smallmatrix}$$
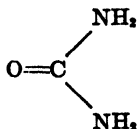
The seven parameters defining the atomic positions for the orthorhombic $CS(NH_2)_2$ have not been satisfactorily determined. Quantitative measurements of intensities of x-ray reflections would probably lead to a complete structure determination. The minimum molecular symmetry is a plane of symmetry (figure 7b), and it is possible that the molecule has the same symmetry as urea. It is probable that the C—S distance is about 1.81 Å. (25). (Compare C—Cl in $C_6H_6Cl_6$ and C_2Cl_6.) In the crystalline state the formula must be the symmetrical one rather than

$$HS—C \begin{smallmatrix} NH \\ \\ NH_2 \end{smallmatrix}$$
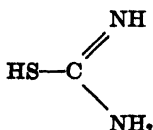
Acetamide, CH_3CONH_2, has been studied, but a complete structure determination was not possible. The rhombohedral unit of structure having $\alpha = 90°17'$, and $a_0 = 8.05$ Å. contains $6CH_3CONH_2$. The molecule is asymmetrical (space-group C_{3v}^6). It is possible that three molecules are associated in $3CH_3CONH_2$ groups.

Some observations have been made on methylurea $CO(NH_2)(NHCH_3)$ and on symmetrical dimethylurea $CO(NHCH_3)_2$ (12). It is possible that each of the molecules of the latter compound has a plane of symmetry as the formula suggests, but this could be ascertained only from a re-examination of the compound.

Hexamethylbenzene (*27*). This is the only aromatic compound for which a satisfactory structure determination has been made. The dimensions of the triclinic unit of structure containing one centrosymmetrical molecule of $C_6(CH_3)_6$ are:

$$a = 9.010 \text{ Å.} \qquad b = 8.926 \text{ Å.} \qquad c = 5.344 \text{ Å.}$$

with

$$\alpha = 44°27' \qquad \beta = 116°43' \qquad \gamma = 119°24'$$

The intensities of reflections were measured quantitatively. The peculiarities in the determined structure factors, arising from a pseudo hexagonal atomic arrangement in (001), allowed the complete determination of the structure even though the atomic positions are defined by eighteen parameters. The space-group is C_i^1.

The atomic arrangement in (001) is shown in figure 8b. Groups of atoms are present. These groups are to be identified as the molecules of $C_6(CH_3)_6$. Their presence demonstrates the existence of the organic molecule as a separate entity in the crystalline state. A molecule not only has a center of symmetry but also possesses a pseudo sixfold axis and a pseudo plane of symmetry, that is, the plane in which all of the carbon atoms are located. Six of the carbon atoms of a particular molecule are arranged in a closed hexagonal grouping. The minimum C—C distances in such a group are 1.42 ±0.03 Å., in agreement with one of the characteristic C—C distances of graphite. The six CH₃ groups of a molecule are arranged as shown in figure 8a. The distance between a carbon atom of the hexagon and its adjacent methyl group is 1.54 ±0.12 Å., in agreement with the minimum C—C distance in the diamond. The coördinates of the atomic positions in the $a\ b$ plane, expressed as fractions of the axes of the unit of structure are:

	(a)	(b)		(a)	(b)
A D	(± 0.071	± 0.182)	G K	(± 0.145	± 0.371)
B E	(∓ 0.109	± 0.073)	H L	(∓ 0.222	± 0.149)
C F	(∓ 0.180	∓ 0.109)	J M	(∓ 0.367	∓ 0.222)

The closest distances of approach of carbon atoms of separate molecules is approximately $d_{(001)} = 3.694$ Å. The projection of two units of structure on (001) is shown in figure 8b. The closest distances of approach between CH₃ groups of separate molecules in (001) are about 4.1 Å.
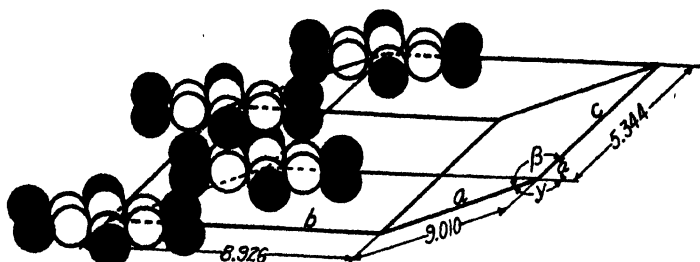
FIG. 8a. HEXAMETHYLBENZENE, $C_6(CH_3)_6$. A PARTIAL REPRESENTATION OF THE UNIT OF STRUCTURE
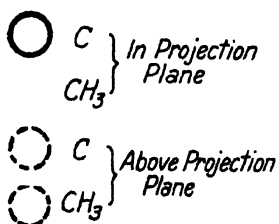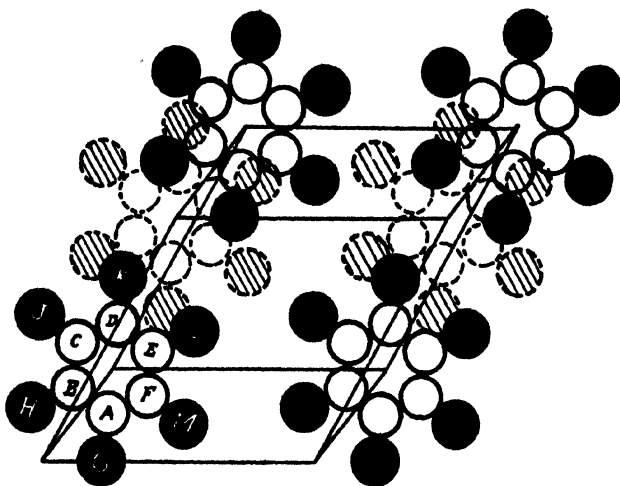
FIG. 8b. HEXAMETHYLBENZENE, $C_6(CH_3)_6$. A PROJECTION OF THE ATOMIC ARRANGEMENT ON (001)

The projection was made from below a.

Methane (28), ethane (29).   Molecular rotation in the solid state (30).   The crystal structures of methane and ethane have been determined from powder photographs at liquid nitrogen temperatures.   Methane has been examined at liquid hydrogen temperatures.   It has a cubic close-packed structure with $a_0 = 6.35$ Å. (figure 9b).
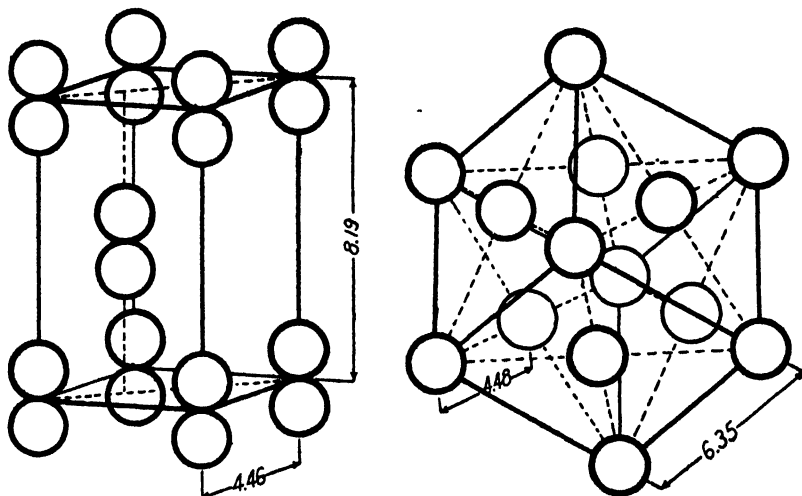
FIG. 9a. ETHANE, C_2H_6. 9b. METHANE, CH_4. UNITS OF STRUCTURE
Carbon atoms only are shown.

The hexagonal unit of structure containing $2C_2H_6$ (figure 9a) has $a = b = 4.46$ Å. and $c = 8.19$ Å.   The positions of the carbon atoms are:

$$\tfrac{1}{3}, \tfrac{2}{3}, u; \ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{2}\text{-}u; \ \tfrac{2}{3}, \tfrac{1}{3}, u + \tfrac{1}{2}; \ \tfrac{2}{3}, \tfrac{1}{3}, \bar{u}$$

The value of u_C is probably .15 − .16, corresponding to a minimum C—C distance of 1.46 − 1.64 Å. (1.55).   The determined association of two atoms to form a molecule need not be assumed in the structure determinations.

In the case of methane it has been pointed out (30), from consideration of the specific heat data, that the molecules are

probably rotating above 20°K and that the structure, a closest packing of spheres, is partially determined by this rotation. Molecular rotation in the solid state is probably a determinative factor in the x-ray diffraction patterns of many crystals. In particular the rotation of the ammonium ion and the water molecule in compounds at ordinary temperatures probably accounts
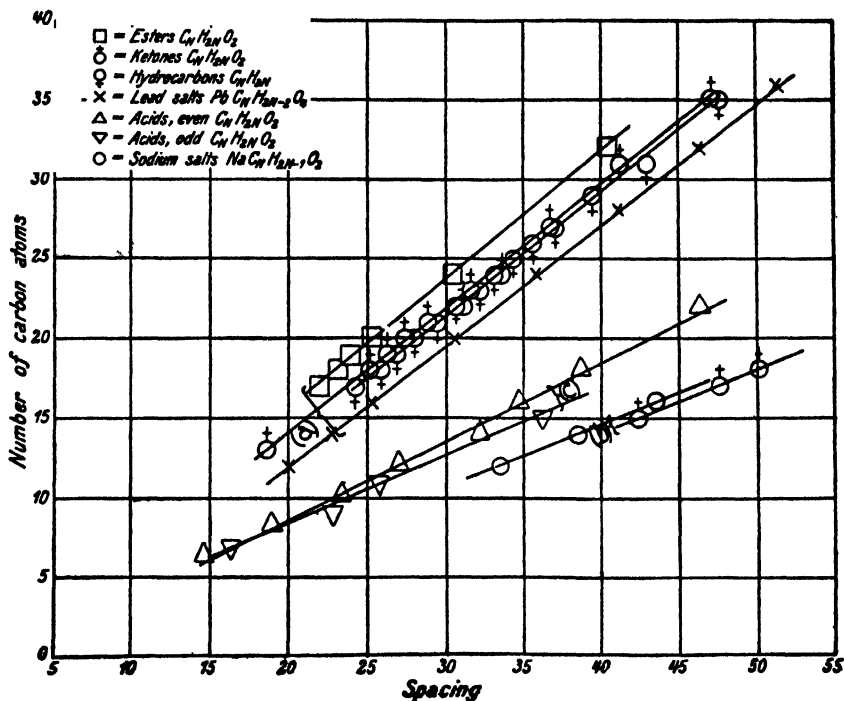
FIG. 10. A PARTIAL GRAPHICAL SUMMARY OF THE LONG SPACING DATA FOR SOME ALIPHATIC COMPOUNDS

for the fact that these molecules occupy positions in crystals with symmetry elements not compatible with those of the non-rotating molecule (30).

The structure of ethane may be considered as a hexagonal "close packing" of ellipsoids of revolution which are the rotating C_2H_6 groups. For this reason it is without significance to compare the intermolecular distances in ethane with those found for

hexamethylenetetramine and hexamethylbenzene. One distance of approach for ethane molecules, a of the hexagonal unit of structure, is 4.46 Å., that is, approximately equal to the distance 4.48 Å. between rotating CH_4 molecules in the methane structure. The closest distance between carbon atoms of separate ethane molecules is about 3.64 Å., in agreement with distances found for the two previously mentioned compounds.

Results obtained from long chain aliphatic compounds. Diffraction patterns from paraffin were noted as early as 1913 (31). Later observations (32) made by reflecting x-radiation from films of sodium oleate solidified on glass surfaces demonstrated the presence of reflections from some plane of great spacing. Syste-
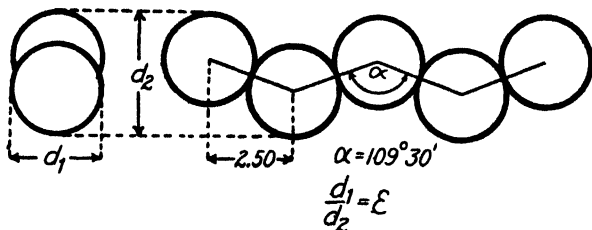
FIG. 11. A POSSIBLE CHARACTERISTIC ATOMIC ARRANGEMENT IN A SATURATED ALIPHATIC HYDROCARBON GROUP

Carbon atoms only are shown.

matic investigations have now been carried out on the x-ray diffraction characteristics of the various members of a number of homologous series.

The published data from long chain aliphatic compounds have usually been obtained from powder photographs and from reflection photographs made from thin films solidified on flat surfaces (glass). The photographs are characterized by the presence of a number of orders of reflection from a plane having a great spacing and by reflections from a few planes having spacings between 2.0 and 5.0 Å. A portion of the long spacing data as listed in the International Critical Tables (33) is summarized in figure 10. The data may be considered to fall into three groups having the following increases in spacing with the addition of

each methylene group: (a) about 1.30 Å.; (b) about 2.60 Å.; and (c) values intermediate between these two.

It was first suggested (34) that the long spacing measurements (a) and (b) were obtained from planes normal to the axes of the hydrocarbon chains, and that the change of this spacing with addition of methylene groups is a measure of the changes or twice the changes in the length of the chain. In case (c) the hydrocarbon chains are inclined to the planes of maximum spacings (35). The diffraction data from a number of compounds may be explained (36) by a coplanar "zig-zag" arrangement of the carbon atoms in a particular hydrocarbon group (figure 11). It is possible for the angle α_0 to be that of a regular tetrahedron.

Investigations have now been carried out upon (1) single crystals or flattened crystalline aggregates of several hydrocarbons (class (a)) and (2) single crystals of several fatty acids (class (c)). The results of these investigations have supported in part the conclusion of the earlier work.

(1) *Nonacosane (37) and other hydrocarbons.* Crystals of nonacosane, $C_{29}H_{60}$, are probably orthorhombic, as is shown by the approximate orthogonality of the crystallographic axes and more definitely by the absence of particular reflections. The dimensions of the unit of structure containing $4C_{29}H_{60}$ are given in table 3. The space-group is C_{2v}^9, in which case the molecule does not have an element of symmetry, or V_h^{16}, in which case the molecule has a plane of symmetry perpendicular to the axes of the chains which are parallel to the c axis of the crystal. It is possible, but not probable, that the substance is monoclinic and the space-group is C_{2h}^5. The molecules are at $x, y, \frac{1}{4}; \bar{x}, \bar{y}, \frac{3}{4};$ $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \frac{1}{4}; \bar{x} + \frac{1}{2}, y + \frac{1}{2}, \frac{3}{4}.$ If the space-group is V_h^{16}, the fifteenth carbon atom must be on the plane of symmetry. The molecule need have no other element of symmetry, but if the carbon atoms have a "zig-zag" arrangement in the chain, it is possible for them all to be in the same plane. This arrangement was assumed in the analysis of the structure, and results were obtained which explained satisfactorily the observed intensities of reflection.

A model of $C_{29}H_{60}$ is shown as figure 12.   The following values were determined:

$$w = 1.62 - 1.23; \quad \phi = 23° - 30°; \quad S = 2.54;$$

$$\psi = 44° - 52°; \quad D_2 = 3.6 - 3.9 \text{ Å}; \quad D_1 = 1.8 - 2.0 \text{ Å}.$$

$$D_3 = \text{about } 4.00\text{Å}; \quad t + x - \alpha_0 = \text{about } 1/7.5.$$
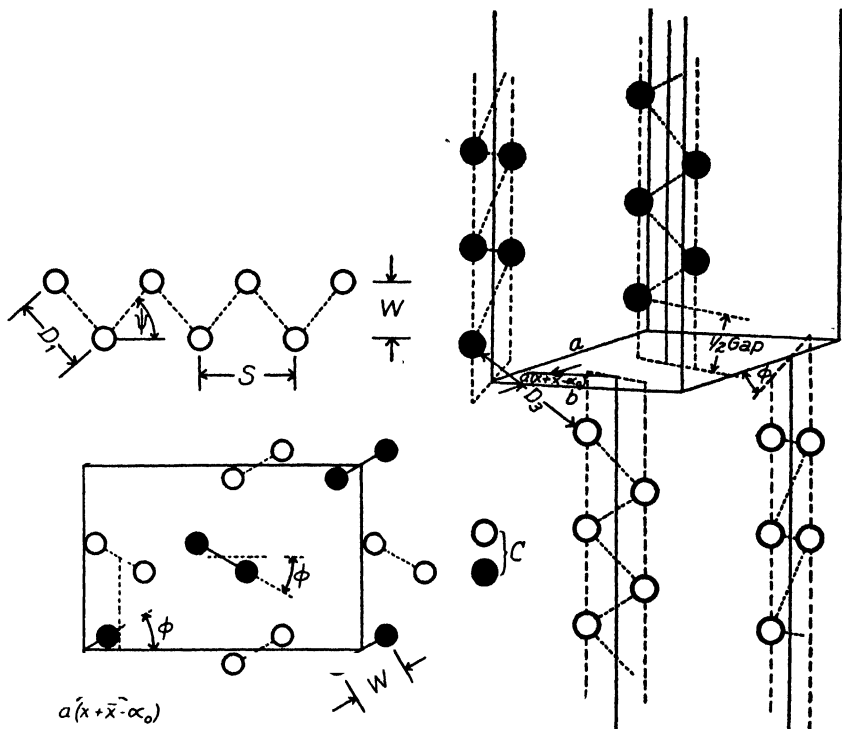
FIG. 12. NONACOSANE, $C_{29}H_{60}$. A PARTIAL REPRESENTATION OF THE STRUCTURE

The lettered designations are discussed in the text.   Carbon atoms alone are shown.

It is to be noted that the values of D_2 and D_3 are approximately the same as those found for simple compounds.   The value D_1, of the minimum distance between scattering centers (assumed to be CH_2 groups) is much greater than the probable value found for simpler compounds (compare C_2H_6).

TABLE 3
Results of x-ray examinations of some fatty acids and aliphatic hydrocarbons

COMPOUND	FORMULA	a	b	c	β	$a \cdot b$	$\dfrac{ab}{\sin\beta}$	$\dfrac{c}{\sin\beta}$	$\dfrac{a}{\sin\beta}$	e
Lauric acid	$CH_3(CH_2)_{10}COOH$	9.76	4.98	36.9	48° 6′	48.6	36.5	27.6	7.32	0.681
Stearic acid	$CH_3(CH_2)_{16}COOH$	5.55	7.38	48.84	63° 16′	40.94	36.6	43.76	4.95	0.671
Behenolic acid	$CH_3(CH_2)_7C:C(CH_2)_{11}COOH$	9.55	4.69	59.10	53° 30′	44.76	36.0	47.51	7.67	0.612
Stearolic acid	$CH_3(CH_2)_7C:C(CH_2)_7COOH$	9.55	4.69	49.18	53° 4′	44.76	35.8	39.28	7.63	0.614
Bromostearic acid	$CH_3(CH_2)_{16}CHBrCOOH$	11.04	4.90	52.88	43° 15′	54.13	37.1	36.23	7.56	0.648
Nonacosane	$CH_3(CH_2)_{27}CH_3$	7.45	4.97	77.2	90°	37.0	37.0	77.2	7.45	0.667

TABLE 4
Results of x-ray measurements for some dicarboxylic acids

ACID	FORMULA	a	b	c	β	MOLECULES IN ELEMENTARY CELL	$ac \sin\beta$	DISTANCE BETWEEN END GROUPS
Adipic	$C_6H_{10}O_4$	10.27	5.16	10.02	137° 5′	2	36.18	3.70
Pimelic	$C_7H_{12}O_4$	9.93	4.82	22.12	130° 40′	4	36.26	3.47
Suberic	$C_8H_{14}O_4$	10.12	5.06	12.58	135° 0′	2	36.24	3.73
Azelaic	$C_9H_{16}O_4$	9.72	4.83	27.14	129° 30′	4	36.22	3.47
Sebacic	$C_{10}H_{18}O_4$	10.05	4.96	15.02	133° 50′	2	35.96	3.65
Brassylic	$C_{13}H_{24}O_4$	9.63	4.82	37.95	128° 20′	4	36.41	3.81
Hexadecanedicarboxylic	$C_{18}H_{34}O_4$	9.76	4.92	25.10	131° 10′	2	36.20	3.62
Oxalic	$C_2H_2O_4$	6.46	7.79	6.02	90°	4		
Succinic	$C_4H_6O_4$	5.07	8.92	5.52	91° 20′	2		
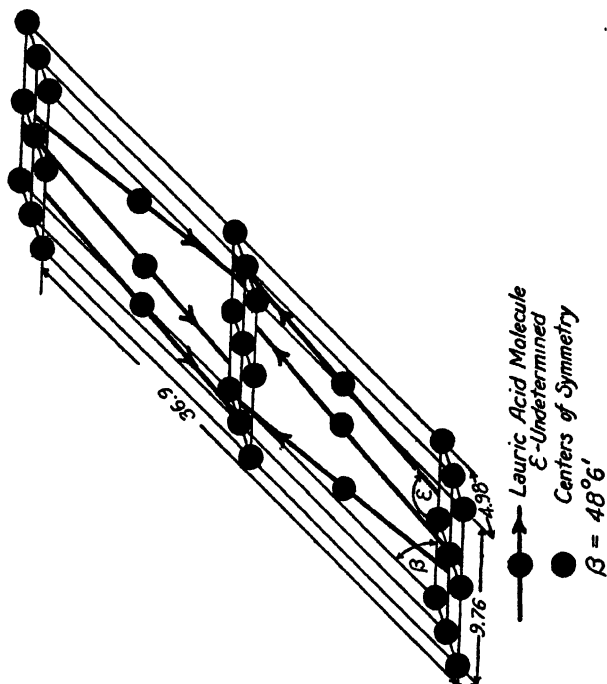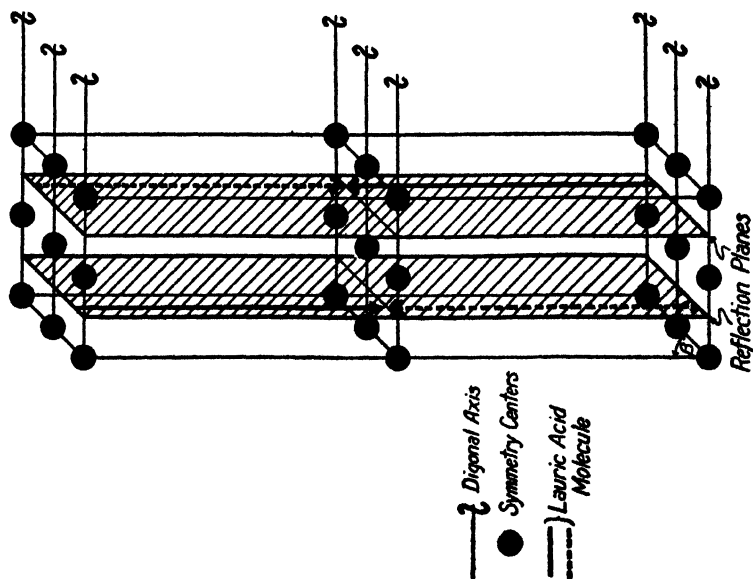
FIG. 13. LAURIC ACID, $C_{11}H_{23}COOH$. THE UNIT OF STRUCTURE SHOWING TWO POSSIBLE MOLECULAR ARRANGEMENTS

Photographs of $C_{29}H_{60}$ made at liquid air temperatures and near the melting point merely show slight alterations in the diffraction patterns as produced by expansion of the lattice. It is improbable that the molecules are rotating at room temperature. Detailed observations have also been made on compressed powders of $C_{35}H_{72}$ and $C_{70}H_{142}$ (?). The results were similar to those obtained from $C_{29}H_{60}$ (33).

A hydrocarbon containing an even number of carbon atoms can not have a plane of symmetry perpendicular to the axis of a "zig-zag" chain. For this reason it is probable that the space-group would be other than V_h^{16} for such compounds, unless the unit of structure contained eight non-equivalent molecules.

(2) *Lauric acid (39), stearic acid (35), bromostearic acid (35), stearolic acid (35), and behenolic acid (35).* The results obtained from these compounds are summarized in table 3. The crystals are all monoclinic prismatic; the point-group is C_2^h. The monoclinic unit of structure for lauric acid, containing $4CH_3(CH_2)_{10}$-COOH, is shown in figure 13. The meaning of the symbols a, b, c, and β used in table 3 are perhaps evident from this figure.

Lauric acid probably has an atomic arrangement derivable from space-group C_{2h}^1 or C_{2h}^2. If the structure is to be derived from one of these space-groups the molecules probably can not be crystallographically identical since the formula does not permit a center of symmetry. Two possible structures are shown in figure 13. In either case the lauric acid molecule has a plane of symmetry perpendicular to the symmetry axis. Structures in which the molecules have centers of symmetry are precluded by the formula of the compound. A spiral structure of the chain is impossible, and if the molecule has a "zig-zag" configuration the carbon atoms must all lie in the plane of symmetry. The great length of the c axis suggests that the hydrocarbon chains are approximately parallel to that axis.

Stearic acid too has a structure isomorphous with point-group C_2^h, and it is assumed that the molecule has a plane of symmetry. For all the acids studied the value of $a\,b\,\sin\,\beta$, which is supposedly the cross-sectional area occupied by two molecules, is approximately constant, and is the same as for the hydrocarbon non-

acosane, $C_{29}H_{60}$. It has been suggested that ϵ, i.e. $\dfrac{a \sin \beta}{b}$ or $\dfrac{b}{a \sin \beta}$ depending upon whether $b > a \sin \beta$ or $b < a \sin \beta$, is a measure of d_1/d_2 in the hypothetical chain shown in figure 11. That this is probably not the case can be ascertained by an inspection of figure 12. It is to be noted, however, that in all cases save that of stearic acid, ϵ is expressed as $\dfrac{b}{a \sin \beta}$. The fact that the b axis of stearic acid is approximately equal to $a \sin \beta$ for lauric acid makes it very difficult to see exactly what structural relationships they have in common. It is possible that stearic acid only simulates monoclinic symmetry.

From the indicated variations of the angle β (table 3) it perhaps can be seen that no direct significance could be attached to the long spacing measurements ($c \sin \beta$) for the fatty acids listed in figure 10. If it is assumed that the axes of the hydrocarbon groups are approximately parallel to the c axis of the crystal, then the increase in the length of this axis might be used as a measure of the increase in chain length on addition of methylene groups. This change between lauric and stearic acids is 11.9 Å., corresponding to about 1.98 Å. for each methylene group. This value is markedly smaller than that of the compounds of type (a) shown in figure 10, for which the more complete examination of nonacosane suggests an increase of 2.5 Å. in the length of two hydrocarbon chains upon addition of a methylene group. It would seem that the molecules of the fatty acids do not have their chain axes accurately parallel to the c axes of the crystals.

Aliphatic dicarboxylic acids (40). The results of examination of a number of aliphatic dicarboxylic acids are shown in table 4. The crystals are all monoclinic and it is probable that the space-group is C_{2h}^5. The acids with an even number of carbon atoms in the chain have but two molecules in the unit of structure. In such cases the space-group symmetry requires each molecule to have at least a center of symmetry; this is possible from the chemical formula, since the end groups are similar (see figure 14).

The acids with an odd number of carbon atoms in the chain

have four molecules in the unit of structure which are not required to have an element of symmetry. This might be expected since the formula will not admit of a center of symmetry. The values of a c sin β (table 4) are the same for these compounds as for the fatty acids and the hydrocarbons listed in table 3. This suggests that this constant area is a characteristic of two hydrocarbon chains and is unaffected by the presence of dissimilar end groups or by atoms such as bromine.

As is the case for monocarboxylic acids, no direct significance can be attached to the values of the maximum spacings (c sin β),
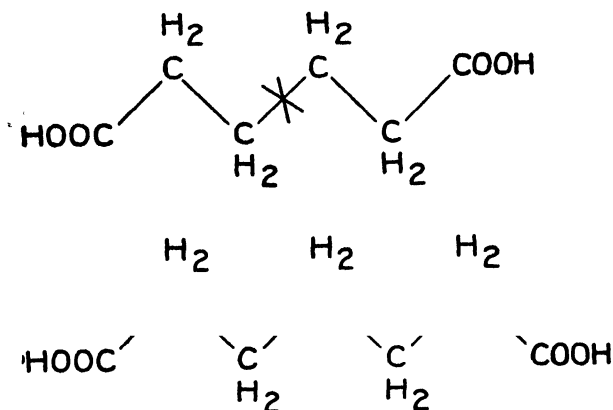
FIG. 14. DICARBOXYLIC ACIDS. STRUCTURAL FORMULAS

The possible symmetry center is indicated by the cross mark.

although the variations in β are quite small. The dicarboxylic acids, however, clearly illustrate the characteristics (a) and (b) of figure 10. The increase in the length of the c axis between adipic acid and hexadecanedicarboxylic acid (even numbers of carbon atoms) is 15.08 Å., corresponding to 1.25 Å. for each added methylene group (a). The change in the length of the c axis between pimelic acid and brassylic acid corresponds to an increase of 2.65 Å. for each CH_2 group. The axes of the hydrocarbon chains are probably closely parallel to the c axes of the crystals. The suggested separations of the end groups of different molecules are listed in table 4; these distances are approximately the same as those found for simple compounds.

Observations have also been made on a series of mono-*n*-alkyl-malonic acids, di-*n*-alkylmalonic acids and acid amides (41). Single crystals were not used.   Measurements have been made on single crystals of oxalic acid (42), and of succinic acid (43).   These structures are not to be compared with those discussed above since their properties are more dependent upon the carboxyl groups.

Alkylammonium halides.   Molecular rotation in the solid state. X-ray investigations have been carried out on single crystals of a number of primary (44, 45), tertiary (46), and quaternary (47, 48, 49) alkylammonium halides, tetramethylammonium per-chlorate and permanganate (50), and some alkylammonium chlorostannates and platinates (51).   These compounds have structural characteristics similar both to ionic inorganic compounds and to molecular organic compounds.   A few typical structures are discussed below.

The results are best exemplified by primary *n*-amylammonium chloride, $C_5H_{11}NH_3Cl$ (30, 44, 52).   This compound is tetragonal. A straightforward analysis of the x-ray data obtained at room temperatures leads to the conclusion that the unit of structure contains $2NH_3C_5H_{11}Cl$ and has $a = b = 5.01$ Å. and $c = 16.69$ Å. The Cl, N, and C atoms are at $0\frac{1}{2}u$, $\frac{1}{2}0\bar{u}$ with $u_{Cl} =$ about .095. The absence of reflections in odd orders from planes $(hk0)$ with $(h + k)$ odd and the intensities of reflections from other planes such as (200) require the carbon atoms of the C_5H_{11} group to scatter x-radiation as if they were arranged colinearly in each group.   The determined atomic arrangement is shown in figure 15, in comparison with that of ammonium chloride.

It has been pointed out (30) that this result, that is quite in-compatible with the results obtained from other long chain aliphatic compounds, might arise from rotation of the molecule about its long axis at room temperatures in the solid state.   Photographs made at liquid air temperatures support this prediction and indicate that the true unit of structure contains $4NH_3C_5H_{11}Cl$ and that it has the approximate dimensions $a = b = 7.0$ Å., $c =$ about 16.6 Å.   A possible resulting atomic configuration is shown in figure 15 (it is assumed that the crystals are tetragonal

at liquid air temperatures). This has not yet been accurately determined. The C—C distance along the chain axis is probably about 1.25 Å., in agreement with the data from other long chain
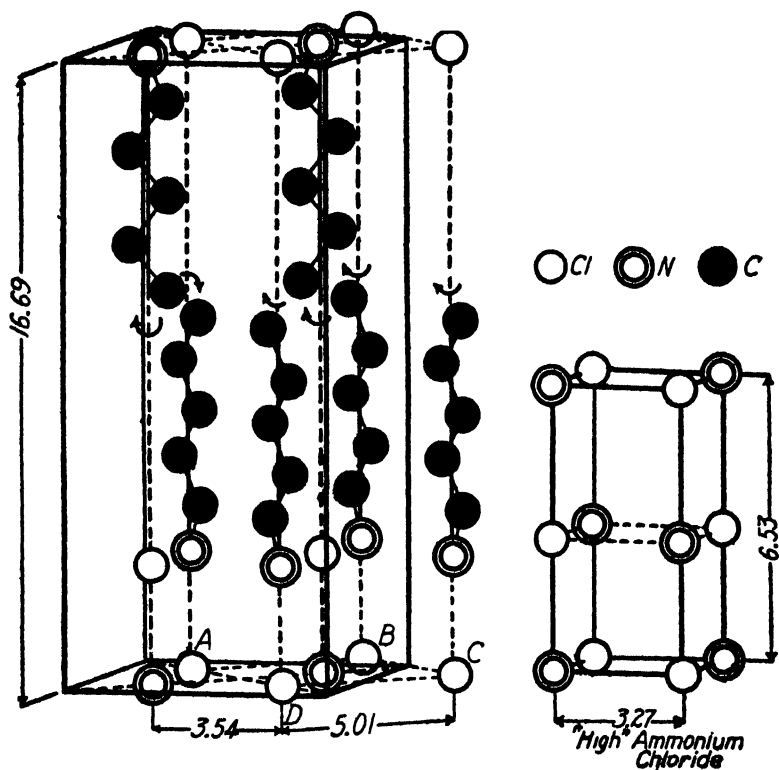
FIG. 15. PRIMARY n-AMYLAMMONIUM CHLORIDE, $NH_3C_5H_{11}Cl$. A REPRESENTA-
TION OF THE TRUE UNIT OF STRUCTURE AND OF THE PSEUDO UNIT DUE TO
MOLECULAR ROTATION, WHICH IS INDICATED BY ARROWS

The positions of the carbon atoms are in part hypothetical. A portion of the unit of structure of "high" ammonium chloride is shown for comparison.

compounds, and it is possible that the C—C separation is about 1.54 Å.

The ionic characteristics of the structure of primary amylammonium chloride suggest that in the crystals at room temperatures the nitrogen atoms are on the axes of the hydrocarbon

chains. The value of $a\ b\sin\beta$ (for the smaller unit of structure) is approximately 25.0 Å., but it is hardly to be compared with the values listed in table 3 since it seems rather to be determined by salt-like properties of the compound, such as the separation of the RNH_3^+ ion and the Cl^- ion. This large area occupied by a *single* hydrocarbon chain (figure 15) probably reduces the crystal forces and the geometrical constraints sufficiently to allow molecular rotation at room temperatures. The minimum distance
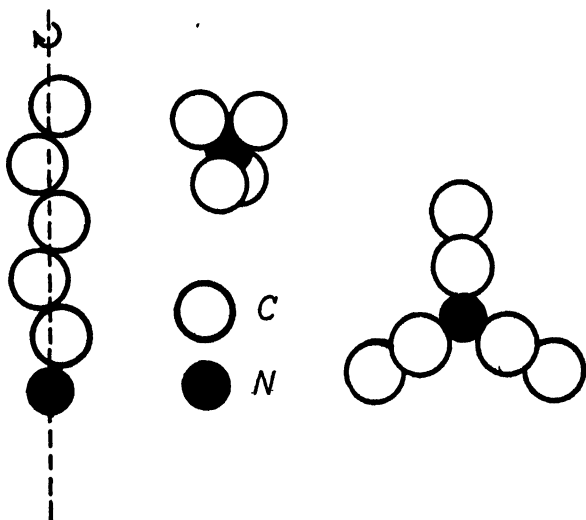
FIG. 16. $(NH_3C_5H_{11})^+$, $N(CH_3)_4^+$, AND $NH(C_2H_5)_3^+$. MOLECULAR CONFIGURATIONS

between the end groups of separate hydrocarbon molecules might well be approximately the same as that found for other organic molecules. The configuration of a single $(NH_3C_5H_{11})^+$ group is shown in figure 16.

The crystal structures of the primary *n*-butyl- to heptyl-ammonium halides, and primary methylammonium bromide and iodide are similar to that of sodium chloride or "high" ammonium chloride, as may perhaps be seen by inspection of figure 15. The structures of primary methylammonium chloride and the primary propylammonium halides (figure 17) are more closely

related to that of caesium chloride or "low" ammonium chloride. Molecular rotation in the solid state probably modifies the structures of these compounds at room temperatures.

A representation of the unit of structure of $N(CH_3)_4Cl$ (47) is shown in figure 17, in comparison with that of ammonium chloride. The structures of the other tetramethylammonium com-
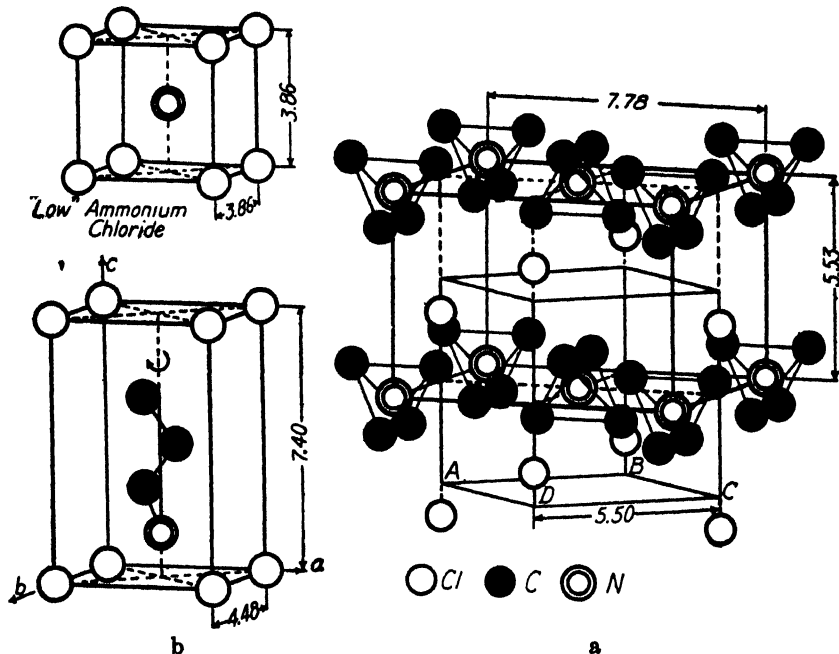
Fig. 17a. Tetramethylammonium Chloride, $N(CH_3)_4Cl$. The Unit of Structure Showing the Pseudo Sub Unit (ABCD as Base) which is to be Compared with the Unit of Structure of "low" Ammonium Chloride

Fig. 17b. Primary Propylammonium Chloride, $NH_3C_3H_7Cl$. The Pseudo Unit of Structure with Indicated Molecular Rotation

pounds are similar. In these compounds the nitrogen atom of each alkylammonium group is surrounded by four methyl groups at the corners of a tetragonal bisphenoid (figure 17). The configuration of a $NH(C_2H_5)_3{}^+$ group as derived from the determined crystal structures of the triethyl ammonium halides (46) is shown in figure 16. It is possible that, in both these types of

compounds, the alkyl groups are rotating in the crystalline state at room temperatures, but it is improbable that the $N(CH_3)_4^+$ and $NH(C_2H_5)_3^+$ groups as a whole are rotating.

The group configurations shown in figure 16 are probably to be found in such compounds as substituted ammonium alums and in the alkylammonium halogen stannates and platinates (51).

Further discussion of results obtained from some long chain compounds. "Long spacing" measurements for hydrocarbons and related compounds have permitted certain structural deductions even though complete structure determinations could not be made. In the first place the hydrocarbon chain is very long in one direction and is not in part folded back on itself. Ketones, such as $RCOCH_3$, show an increase of about 2.5 Å. in the "long spacing" for the addition of each (CH_2) group (53). This suggests (note the structure of lauric acid) that these groups are sufficiently polar to cause an end-to-end orientation of two molecules. A ketone, $RCOR'$, must have an extended structure rather than a folded one, such as

$$\begin{array}{c} R \\ \diagdown \\ CO \\ \diagup \\ R' \end{array}$$
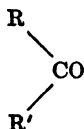
It has been shown that there are probably two or more modifications of the fatty acids (55) and of the saturated aliphatic hydrocarbons (56).

It has been suggested (54) that the well-known oscillations in properties between compounds with even and with odd numbers of carbon atoms arise in part from the "zig-zag" nature of the grouping. The alterations of the chemical relationships in dicarboxylic acids (57) are probably to be accounted for by their derived structures (40).

Observations made on polymerized formaldehyde products (58, 59) show that the condensation products are greatly elongated in one direction. A number of diacetate derivatives of polymerized formaldehyde

$$CH_3\!-\!\!\overset{\displaystyle C}{\underset{\displaystyle O}{\|}}\!\!-\!(OCH_2)_x\!-\!O\!-\!\overset{\displaystyle C}{\underset{\displaystyle O}{\|}}\!-\!CH_3$$
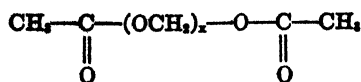
TABLE 5

Unit of structure and space-group determinations for some organic compounds

COMPOUND	SYMMETRY	a	b	c	β	SPACE GROUP	MOLECULES PER UNIT CELL	MINIMUM MOLECULAR SYMMETRY	REFERENCES
Naphthalene	Monoclinic	8.34	5.98	8.68	122° 44'	C_{2h}^5	2	Center of symmetry	(61, 62, 63)
Anthracene	Monoclinic	8.58	6.02	11.18	125° 0'	C_{2h}^5	2	Center of symmetry	(61, 62, 63)
Diphenyl	Monoclinic	8.22	5.69	9.50	94° 46'	C_{2h}^5	2	Center of symmetry	(64, 69)
Phenanthrene	Monoclinic	8.60	6.11	19.24	98° 15'	C_{2h}^5	4	None	(64)
Fluorene	Monoclinic	8.48	5.73	19.24	101° 53'	C_{2h}^5	4	None	(64)
Dimesityl	Monoclinic	8.21	8.58	22.25	96° 30'	C_{2h}^5	4	None	(69)
Dibenzyl	Monoclinic	12.82	6.18	7.74	115° 54'	C_{2h}^5	2	Center of symmetry	(64)
Stilbene	Monoclinic	12.42	5.73	16.0	114° (approx.)	C_{2h}^5	4	None	(64)
Indigo	Monoclinic	11.00	5.8	10.09	107° 30'	C_{2h}^5	2	Center of symmetry	(68)
d-Glucose	Orthorhombic	10.40	14.89	4.99	90°	V^4	4	None	(65)
α-Methyl glucoside	Orthorhombic	11.29	14.72	5.29	90°	V^7	4	None	(66)
d-Fructose	Orthorhombic	8.06	10.06	9.12	90°	V^4	4	None	(65)
α-Methyl mannoside	Orthorhombic	9.44	10.06	9.33	90°	V^7	4	None	(66)
d-Cellubiose	Monoclinic	5.00	13.2	11.1	90°	C_2^3	2	None	(65)

o-Dinitrobenzene......	Monoclinic	7.95	13.0	7.45	112° 7'	C_{2h}^5	4	None	(67)
m-Dinitrobenzene....	Orthorhombic	13.3	14.2	3.82	90°	V_h^{16}	4	Probably plane of symmetry; center of symmetry	(67)
p-Dinitrobenzene...	Monoclinic	11.3	5.55	5.8	92° 18'	C_{2h}^5	2	Center of symmetry	(67)
Hexachlorobenzene...	Monoclinic	8.06	3.84	16.6	116° 50'		2		(12)
Hexabromobenzene...	Monoclinic	8.44	4.04	17.3	116° 30'		2		(12)

with 8–19 CH_2O groups show an increase in the long spacing from 23.7 Å. to 43.7 Å., corresponding to about 1.9 Å. for each CH_2O group. Preliminary observations on a number of "polyenes," C_6H_5—C=C—C=C$\cdots C_6H_5$ (60), indicate that the long spacing increases about 1.5 Å. for each added —C=C—group; this suggests that the arrangement might be

$$
\begin{array}{ccc}
-\text{C} & \text{C}-\text{C} \\
\parallel & \parallel & \parallel \\
\text{C}-\text{C} & \text{C}- \\
\end{array} \ .
$$
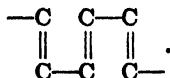
It is probable in these cases that the increase in the "long spacing" is not a true measure of the change in the length of the chain upon addition of groups (note the fatty acids).

UNIT OF STRUCTURE, SPACE-GROUP, AND MOLECULAR SYMMETRY DETERMINATIONS

The complexity of the structures of most organic compounds and the lack of guiding principles to aid in their elucidation has prevented a more thorough analysis than a unit of structure and space-group determination in some cases. Efforts have been made to detect structural similarities from the dimensions of the units of structures of related compounds. Some instances in which such a method has met with an element of success are described below.

Aromatic hydrocarbons

The results obtained from a number of aromatic hydrocarbons are listed in table 5. In each case the space-group is C_{2h}^5. The units of structure contain four asymmetric molecules or two molecules that must at least have a center of symmetry. Thus naphthalene, anthracene, diphenyl and dibenzyl have at least a center of symmetry. Stilbene and dimesityl with symmetrical formulas do not necessarily have an element of symmetry. The values of a, of $a \sin \beta$, and of b, and therefore of $ab \sin \beta$, are similar for naphthalene, anthracene, diphenyl, phenanthrene and fluorene.

It has been suggested (63) that the change in the length of the c axis, 2.50 Å., between naphthalene and anthracene is a measure

of the width of the benzene ring. It is said that a calculated periodicity of scattering matter along the *c* axis supports this suggestion. An effort has been made to determine these structures (61). Simplifying assumptions were made to reduce the fifteen parameters for anthracene to four. The structure determined, in which the benzene ring had characteristics similar to aliphatic compounds, was said to be compatible with the experimental data. Later work, however, indicates that the correct structure is one in which all of the atoms of a particular
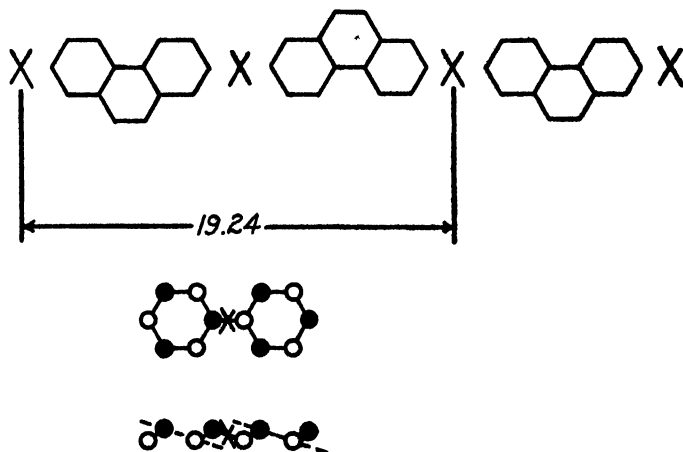
FIG. 18. STRUCTURAL FORMULAS FOR PHENANTHRENE AND FOR DIPHENYL
Centers of symmetry are indicated by cross marks.

molecule are in one plane (61a). This is in agreement with the results obtained from the structure determination of hexamethylbenzene (27), which is a more complete structure determination.

A close similarity is to be observed in the values of *c* or of *c* sin β for fluorene, phenanthrene, and diphenyl; the values of *c* sin β are 2 × 9.42 Å., 2 × 9.52 Å., and 9.45 Å., respectively. The suggestion has been made (64) that the phenanthrene molecules are arranged along the *c* axis as shown in figure 18. The similarities between these compounds and naphthalene and anthracene suggest that the molecules are oriented relative to the crystallographic axes, approximately as shown in figure 19. The actual

dimensions of the unit of structure are not relative measures of the molecular dimensions.

The dimensions of the units of structure for stilbene and dibenzyl are similar in the length of the b axis to those of the compounds mentioned above. In all of the above cases the formulas are probably extended rather than folded back in part.
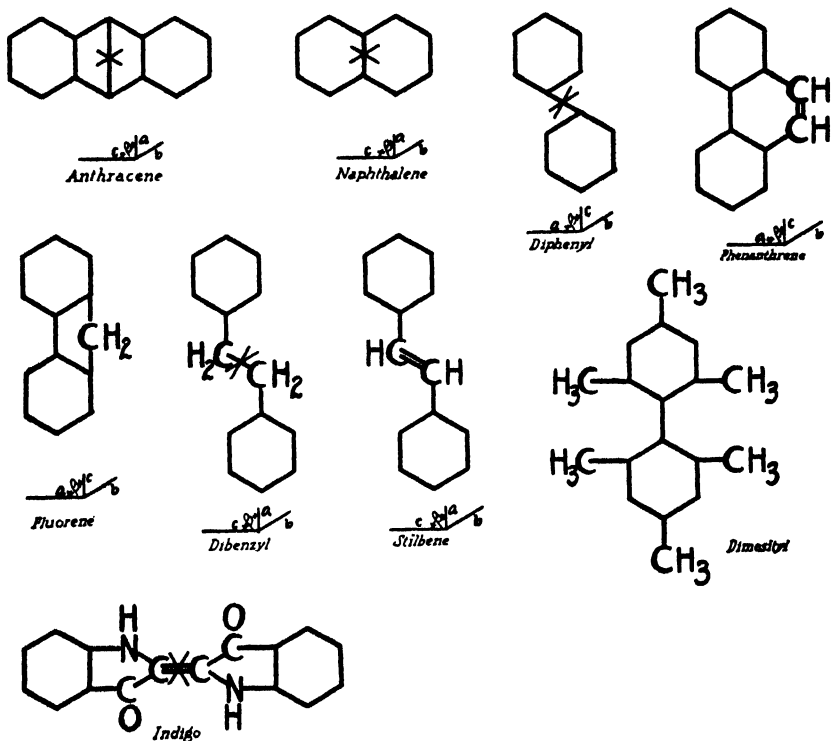
FIG. 19. STRUCTURAL FORMULAS OF A NUMBER OF AROMATIC HYDROCARBONS

Centers of symmetry are indicated by cross marks. Possible positions of the axes relative to the molecules are shown schematically.

Sugars and sugar-like compounds

The units of structure of d-glucose, d-fructose, d-cellobiose (65) α-methylglucoside (m.p. 110°C.), and α-methylmannoside (66) are listed in table 5. In each case the molecule, as might be expected from its chemical formula, does not necessarily have an

element of symmetry. Close similarities are to be noted in the dimensions of the units of structure of d-glucose and α-methylglucoside, and of d-fructose and α-methylmannoside. The volumes of the units of structure of α-methylglucoside and α-methyl mannoside are the same within experimental error; the densities are the same, although the dimensions of the units of structure are markedly different.

Dinitrobenzenes (67)

Unit of structure and space-group determinations have been carried out for o-, m-, and p-dinitrobenzenes (table 5). p-Dinitrobenzene has at least a center of symmetry, as might be expected from its formula. m-Dinitrobenzene has either a center of symmetry or a plane of symmetry; the former can hardly be the case. An inspection of the published data (67) does not show clearly whether the plane of symmetry is perpendicular to the benzene ring as suggested, or whether the benzene ring and the nitrogen atoms, as well as perhaps the oxygen atoms, are in the plane of symmetry. In either case the length of the c axis, 3.82 Å., is a measure of the closest distance of approach between two molecules of separate units of structure. This distance is approximately the same as the closest distances of approach between atoms of separate molecules of other organic compounds (table 7).

Compounds CR₄

The minimum molecular symmetry has been determined for some tetrasubstituted products of methane. Pentaerythritol $C(CH_2OH)_4$ (70), pentaerythritol tetraacetate $C(CH_2OCOCH_3)_4$ (71) and the tetramethyl ester of methanetetracarboxylic acid $C(COOCH_3)_4$ (72) probably have molecular symmetry corresponding to that of the point-group S_4. The substituted groups are arranged tetrahedrally around the central carbon atom. In each of the above cases the tetragonal unit of structure contains $2CR_4$, and the space-group is S_4^2, C_{4h}^4, and C_{4h}^3 respectively. The results are in agreement with the accepted tetrahedral distribution of the valences of carbon in aliphatic compounds.

Observations on dibenzalpentaerythritol (73) indicate that

the molecule must have three twofold axes which are perpendicular one to the other, corresponding to the symmetry of the point group V. The hexagonal unit of structure contains $3C_{19}H_{20}O_4$;
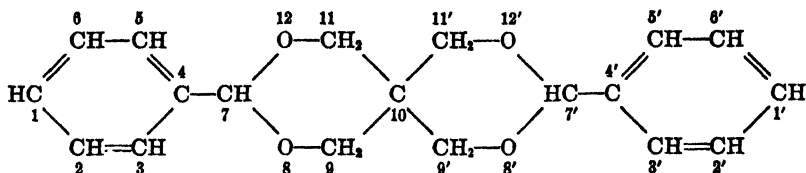
and has $a = b = 6.03$ Å., $c = 36.7$ Å. The space-group is D_6^4. The molecule has a twofold axis along which the atoms designated as 1, 4, 7, 10, 7', 4' and 1' must be placed. The constituents of the benzene ring (1, 2, 6, 4; 4, 3, 5, 1; 4', 3', 5', 1'; 1', 2', 6', 4') must in each set be in a plane, as must also be the atoms 4, 7, 8, 12; 4', 7', 8', 12'. It is possible for all of the atoms of one molecule to be in a plane. These results might in part arise from molecular rotation in the solid state, but the symmetry requirements of the molecule do not suggest such an explanation.

Crystals of pentaerythritol tetraformate (74) have been examined. The orthorhombic unit of structure containing eight molecules has $a = 19.80$ Å., $b = 9.90$ Å., $c = 11.70$ Å. The molecule does not necessarily have an element of symmetry.

Cellulose and other fibrous materials

A fiber x-ray diagram is obtained from an aggregate of crystals or crystallites of a particular material which have some common parallel crystallographic direction. Such a diagram was first noted for hemp fibers in 1913 (75). Investigations have now been carried out on a number of fibrous organic materials—cellulose, hair, muscle, nerves, etc. The characteristics of the fiber diagrams give some indications of the physical properties of the materials.

Attempts have been made to determine the structure of the cellulose residue $(C_6H_{10}O_5)_n$ from ramie fiber diffraction data (76, 77). The spacings of the observed interference pattern can best be explained by a monoclinic unit of structure containing $4C_6H_{10}O_5$, having $a = 8.3$ Å., $b = 10.3$ Å. (fiber axis), $c = 7.9$ Å.,

and β = about 84°.   This small number of $C_6H_{10}O_5$ groups in the unit of structure is hardly in conflict with the known high molecular weight of cellulose, since it is probable that only a periodicity along the fiber axis is determined from the diffraction data.   The postulated atomic arrangements in the glucose residue of ramie (76, 77) are hardly to be emphasized, since even the structure of crystalline glucose is yet unknown.

TABLE 6
Interatomic distances in some organic compounds

DISTANCE	COMPOUND	VALUE IN Å.
C—I	CHI_3	>1.94 (2.10)
C—Br	$C_6H_6Br_6$	1.94
	C_2Br_6	1.97
C—Cl	$C_6H_6Cl_6$	1.81
	C_2Cl_6	1.81
	CCl_4	1.91
C—N	$C_6H_{12}N_4$	1.44
C—O	$CO(NH_2)_2$	1.25 ±0.17
C—S	$CS(NH_2)_2$	1.81 (?)
C—C	C_2H_6	1.55 ±0.09
	$C_6(CH_3)_6$	1.54 ±0.12
	Long chain compounds	1.54
	Diamond	1.54
C—C	Graphite	1.44
	$C_6(CH_3)_6$	1.42 ±0.03
C—H	CH (band spectra)	1.13
N—H	NH (band spectra)	1.08

GENERAL DISCUSSION

It was pointed out in the introduction that complete crystal structure determinations of some organic compounds indicate the presence of groups of atoms in such compounds.   These groups, which are the chemical molecules, are characterized by certain minimum distances of approach between separate atoms within the groups, which are markedly smaller than the shortest distances between the atoms of different groups.   The interatomic distances within the molecules, as determined from a few compounds that have been discussed, are listed in table 6.   The

values are quite constant but, on account of the wide limitations of parameter values, minor variations could not necessarily be detected. It is expected that these values are approximately the ones to be found in other organic compounds.

The distances between atoms of separate molecules are not as constant as are those between atoms of the same molecule. Some regularity, however, is to be noted in the values for a number of halogen compounds (see table 2). Results obtained from a few compounds which contain only carbon, hydrogen, nitrogen, and oxygen are given in table 7. The values are quite similar, even though the possible effects produced by the hydrogen atoms in the different compounds might be expected to cause variations.

TABLE 7

Minimum distances of approach between carbon atoms of adjacent organic molecules

COMPOUND	DISTANCE IN Å.
C_2H_6	3.64
$C_6(CH_3)_6$	3.69
$C_6H_{12}N_4$	3.72
$m-C_6H_4(NO_2)_2$	3.82
$C_{29}H_{60}$	3.6–3.9
$C_6H_{10}O_4$–$C_{18}H_{14}O_2$	3.5–3.8
Graphite	3.35

That these values should be greater than those listed in table 6 is perhaps to be expected from the molecular nature of organic compounds, which implies differences between the intermolecular and intramolecular forces. These differences are exemplified by such physical properties as low melting points, high compressibility coefficients, etc., of molecular compounds as compared with ionic ones.

In some cases the heteropolar characteristics of the compound result in certain regularities in the arrangement of molecules within the structures. This is to be noted in urea and in some of the halogen compounds which have been studied. It is perhaps also true of nitro derivatives of benzene. Such compounds usually have melting points which are comparatively higher than those of other organic substances.

The determined atomic arrangements in aliphatic compounds are in agreement with the concept of a tetrahedral distribution of the carbon valencies. For reasons necessitated by the structure analyses the compounds examined have usually been quite symmetrical ones. In these cases a carbon atom could have a regular tetrahedral distribution of its valencies, but such an arrangement is not necessarily general. One might expect that if several dissimilar atoms are connected to the same carbon atom, the departure from a regular figure might be quite marked. This concept, however, is not supported by any results yet obtained.

In graphite and hexamethylbenzene the three directions in which a carbon atom is surrounded most closely by other atoms are all in the same plane. It is possible that this arrangement is a characteristic one for aromatic compounds. The tetrahedral distribution of carbon valencies is probably to be found only in aliphatic compounds.

The determined minimum molecular symmetries of organic compounds are usually in agreement with expectations based on the structural formulas. In the case of indigo, however, the presence of a center of symmetry was not necessarily expected. The symmetry of dibenzalpentaerythritol could be compatible both with the requirement of "plane" benzene rings and with the tetrahedral configuration of the aliphatic carbon atoms. It is to be emphasized that the symmetry determined from the x-ray diffraction data is the minimum one, except in a few special cases.

Attempts have been made to determine the atomic configurations of special isomers, such as maleic and fumaric acids and of optically active compounds such as d- and l-tartaric acids. These attempts have not been very successful. The diffraction characteristics of optical isomers of a compound are necessarily the same since reflection of x-radiation adds an effective center of symmetry. Optically active compounds always crystallize in forms belonging to one of the eleven crystal classes which possess no planes of symmetry.

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CARBON SUBOXIDE

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Oxides of carbon other than carbon dioxide and carbon monoxide have received very little mention in American chemical literature. This review of carbon suboxide, C_3O_2, and its properties will attempt to bring up to date the information available on this interesting substance, which is now being investigated in the chemical laboratory of the University of Minnesota.

HISTORICAL

Brodie (1) in 1873 submitted carbon monoxide to the action of the electric current and found that the volume of gas contracted with the formation of carbon dioxide and of a transparent red-brown film on the walls of the tube. This film dissolved completely in water to give a strongly colored solution with an intensely acid reaction. Analysis showed the substance to be an oxide of carbon, but samples from different experiments did not have the same composition. Brodie reported two oxides, C_4O_3 and C_5O_4. He suggested that a series of "oxycarbons" existed which would be analogous to the series of hydrocarbons of the acetylene series. On this basis C_4O_3 was analogous to C_4H_6 or crotonylene, and C_5O_4 analogous to C_5H_8 or valerylene.

Berthelot (2) repeated the work of Brodie and found that this brown oxide when heated decomposed to form carbon dioxide, carbon monoxide and a new oxide $C_{16}O_6$. He believed that a series of carbon suboxides (3) were formed from the reactions:

$$n\ CO \rightarrow C_n O_n$$

$$C_n O_n \rightarrow C_{(n-1)} O_{(n-2)} + CO_2$$

479
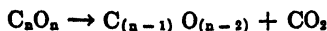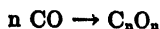
He reported (4) the possibility of the first member of the series, C_2O.

The splitting and dehydration of esters of carbamic acid by phosphorus pentoxide was well known, such as the formation of phenyl isocyanate from the ethyl ester of carbanilic acid:

$$C_6H_5NHCOOC_2H_5 \rightarrow C_6H_5N=C=O + C_2H_5OH$$

Diels and Wolf (5) tried this reaction on nitrogen-free esters in the hope of preparing a new class of compounds. When diethyl malonate was treated in this manner they obtained ethylene, water and a gas with a highly pungent odor, which on analysis was found to have the formula C_3O_2. A vapor density determination confirmed this as the molecular formula. This substance they named carbon suboxide.

Berthelot (4) objected to the use of the name "carbon suboxide" for this compound on the basis that the name "suboxide of carbon" represented a whole family of compounds and no one member in particular. Micheal (11) also stated that the name "carbon suboxide" was not fortunately chosen since it did not express the composition of the compound and was also suitable for the compound C_2O. He suggested the name "tricarbodioxide." Otto Diels (12) replied that other names, as "dicarbonylmethane" or "dioxoallene," were also correct, but that they had tried to give the compound a simple name that showed that it consisted only of carbon and oxygen, as is emphasized in the names "carbon dioxide" and "carbon monoxide." From this viewpoint the name chosen seemed appropriate, and as it had already gone into the scientific literature no attempt was made to change it.

PREPARATION OF CARBON SUBOXIDE

Diels and Wolf (5) prepared the suboxide by treating diethyl malonate with a large excess of phosphorus pentoxide and heating the mixture to 300°C. The reaction took place as follows:

$$CH_2(COOC_2H_5)_2 \rightarrow 2 H_2O + 2 C_2H_4 + C_3O_2$$
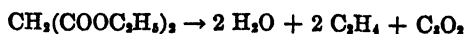
The products were drawn by a vacuum through a receiver cooled in ice to remove any ester which was carried over, and then into a

receiver cooled with liquid air where the ethylene and carbon suboxide were condensed. After the reaction was over, the latter flask was connected to a U-tube with a small bulb in the center. This was cooled with a liquid air-alcohol mixture at $-60°$ to $-70°$, and the receiver which contained the mixed product was removed from the liquid air. The ethylene passed off while the carbon suboxide was condensed in the small bulb. No yield was reported by these authors.

Diels and Meyerheim (8) found that other esters of malonic acid, such as the dimethyl, dibenzyl, and diphenyl esters, yielded carbon suboxide when treated with an excess of phosphorus pentoxide. Other compounds, such as oxalacetic ester, $C_2H_5OOC \cdot CO \cdot CH_2COOC_2H_5$, and methenyltricarboxylic ester, $CH(COOC_2H_5)_3$, also gave carbon suboxide when treated with phosphorus pentoxide. Free malonic acid yielded carbon suboxide when heated with phosphorus pentoxide, but the yields were low (about 10 to 12 per cent) because of the splitting of the malonic acid into acetic acid and carbon dioxide. Stock and Stoltzenberg (18) showed that the low yield by this method was due not to the decomposition of malonic acid into acetic acid and carbon dioxide, but to the polymerization of the carbon suboxide formed. They devised a new apparatus in which they were able to increase the yield to 25 per cent. However Diels (19) considered the apparatus too elaborate for use in this preparation.

Staudinger and Klever (10) applied methods used for ketenes to the preparation of carbon suboxide. Upon the treatment of dibromomalonyl bromide in ether solution with metallic zinc the following reaction occurred:

$$COBr \cdot CBr_2 \cdot COBr + 2\ Zn \rightarrow C_3O_2 + 2\ ZnBr_2$$
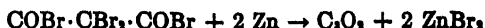
The ether was distilled off, giving an ethereal solution of carbon suboxide. Staudinger and Bereza (14), by treating malonyl chloride with various oxides and salts, such as silver oxide, lead oxide, zinc oxide, silver oxalate and silver malonate, prepared carbon suboxide in yields of from 5 to 10 per cent.

$$CH_2(COCl)_2 + Ag_2O \rightarrow C_3O_2 + 2\ AgCl + H_2O$$
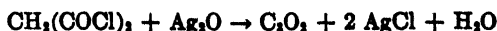
Acid chlorides were found to react with silver malonate to give carbon suboxide in yields of 1 or 2 per cent. It was also found that dibromomalonyl chloride in ether solution reacted with zinc dust, so that by dropping the solution of the acid chloride on the zinc dust at such a rate that the ether boiled vigorously, and by condensing the vapors in a cooled receiver, an ethereal solution of carbon suboxide was obtained which corresponded to an 80 per cent yield.

Ott (17) found that carbon suboxide could be prepared in good yields by the pyrogenic decomposition of diacetyltartaric anhydride or acetoxymaleic anhydride.

$$
\begin{array}{l}
CH_3COO\text{—}CH\text{—}CO \\
\qquad\qquad\qquad\searrow \\
\qquad\qquad\qquad\quad O \rightarrow 2\ CH_3COOH \\
\qquad\qquad\qquad\nearrow \\
CH_3COO\text{—}CH\text{—}CO
\end{array}
$$

$$
\begin{array}{l}
CH_3COO\text{—}C\text{——}CO \\
\qquad\qquad\qquad\searrow \\
\qquad\qquad\qquad\quad O \rightarrow\ CH_3COOH \\
\qquad\qquad\qquad\nearrow \\
\qquad\quad CH\text{—}CO
\end{array}
\qquad
+
\qquad
\begin{array}{l}
C\text{—}CO \\
\ \|\|\qquad\quad\searrow \\
\ \|\|\qquad\qquad\ O \rightarrow C_3O_2 + CO \\
\ \|\|\qquad\quad\nearrow \\
C\text{—}CO
\end{array}
$$
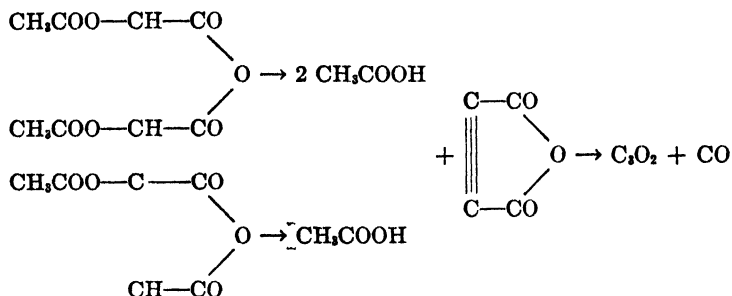
Ott believed that the course of the reaction was the splitting off of acetic acid, which he isolated to the extent of 90 per cent of the theoretical value, and the formation of the anhydride of acetylene diacid, which decomposed into carbon suboxide and carbon monoxide. The diacetyltartaric anhydride may be easily prepared from acetic anhydride and tartaric acid. Using this method Ott (21) obtained a yield of 42.5 per cent of carbon suboxide. Ott and Schmidt (22) designed an apparatus for the carrying out of this reaction in which the vapors of the diacetyltartaric anhydride are passed over a heated platinum filament and the decomposition products are then collected and separated much as in the method of Diels. Using this apparatus they were able to prepare 31.5 grams of diacetyltartaric anhydride, or a yield of 41 per cent of the theoretical amount. Ott (31) reported that carbon monoxide reacted in an ozonizer to give the suboxide.

$$4\ CO \rightarrow C_3O_2 + CO_2$$

CONSTITUTION OF CARBON SUBOXIDE

The constitution of carbon suboxide has given rise to controversy. Diels and Wolf (5) considered that carbon suboxide had the constitution O=C=C=C=O, and gave the following equation for its formation:

$$CH_2(COOC_2H_5)_2 \rightarrow 2\ C_2H_4 + 2\ H_2O + O:C:C:C:O$$
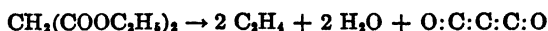
It was shown that carbon suboxide gave reactions similar to those of the ketenes, so they considered it to possess the diketene structure. Micheal (6), however, thought that it would be possible to split off ethylene and water in such a way as to leave a cyclic compound.
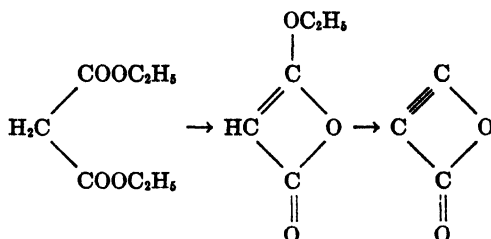
Thus carbon suboxide would be the lactone of β-hydroxypropionic acid. Diels attempted to show, on the basis of the boiling point (8) and the molecular refraction (9) of carbon suboxide, that the constitution which he had suggested for this compound was the correct one. His arguments were refuted by Micheal (11), but again stated by Diels and Blumberg (12).

Staudinger and Klever (10) considered carbon suboxide to be a diketene, and applied methods of preparation which had been used for the ketenes, such as

$$COBr \cdot CBr_2 \cdot COBr + 2\ Zn \rightarrow O:C:C:C:O + 2\ ZnBr_2$$
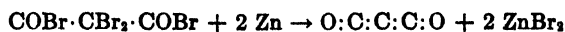
Redgrove (20) calculated the molecular heats of combustion and of formation of the compound according to the two formulas, but no data have ever been given as to these constants.

The diketene formula of Diels is the one usually accepted and written. However, the formula of Micheal has never been proven to be incorrect.

PROPERTIES OF CARBON SUBOXIDE

The physical properties of carbon suboxide are of considerable interest. It is a gas under ordinary conditions, having an unbearable odor like acrolein and mustard oil (5). In small amounts it acts as a lachrymator; in high concentrations it attacks the eyes, nose and breathing organs, giving a feeling of suffocation. The gas is easily condensed to a colorless, refractive, extremely mobile liquid having a boiling point of $+7°$ at 761 mm. pressure (5). Its density at $0°$ compared to water at $0°$ is 1.11 (8). It can be solidified to large crystals which melt at $-107°$ to $-108°$ according to Diels and Meyerheim (8), and at $-111.3°$ according to Stock and Stoltzenberg (18). The vapor pressure was measured by Stock and Stoltzenberg (18) over a range from $-100°$ to $+6°$, and by Edwards and Williams (26) from $-62°$ to $+4°$. The latter also calculated the heat of vaporization from their vapor pressure curve. The molecular refraction of the liquid at $0°$ was found to be 16.6 (9). The refraction and dispersion of the gas were studied at several temperatures (15).

It is in its chemical reactions that carbon suboxide shows its most interesting behavior. Diels and Wolf (5) found that it burns in air to form carbon dioxide.

$$C_3O_2 + 2 O_2 \rightarrow 3 CO_2$$
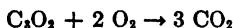
They showed that its reactions with simple substances were those that would be expected from a diketene. It reacts with cold water to form malonic acid.

$$O:C:C:C:O + 2 H_2O \rightarrow CH_2(COOH)_2$$

It reacts with ammonia and aniline at temperatures under $0°$ to form malonamide and malonanilide.

$$O:C:C:C:O + 2 NH_3 \rightarrow CH_2(CONH_2)_2$$
$$O:C:C:C:O + 2 C_6H_5NH_2 \rightarrow CH_2(CONHC_6H_5)_2$$
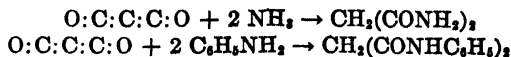
It is reported that the latter reaction may be used for the quantitative determination of carbon suboxide. It reacts with dry hydrogen chloride to form malonyl chloride.

$$O:C:C:C:O + 2 HCl \rightarrow CH_2(COCl)_2$$

It also reacts with bromine to form dibromomalonyl bromide (10).

$$O:C:C:C:O + 2 Br_2 \rightarrow CBr_2(COBr)_2$$

Diels and Lalin (13), using liquid sulfur dioxide at $-30°$ to $-40°$ as solvent, found that carbon suboxide reacted with formic acid giving crystals having the composition $(C_3O_2 + 2 HCOOH)$. With water these crystals gave an equivalent amount of formic and malonic acids, so the compound may be a mixed anhydride of malonic and formic acids, having the formula

$$
\begin{array}{c}
\quad CO\!-\!O\!-\!OCH \\
\diagup \\
CH_2 \qquad\qquad . \\
\diagdown \\
\quad CO\!-\!O\!-\!OCH
\end{array}
$$
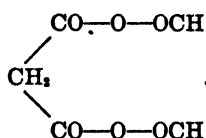
Carbon suboxide and acetic acid also reacted to give a compound having the properties of a mixed anhydride of malonic and acetic acids, whose formula would be

$$
\begin{array}{c}
\quad CO\!-\!O\!-\!OC \cdot CH_3 \\
\diagup \\
CH_2 \qquad\qquad . \\
\diagdown \\
\quad CO\!-\!O\!-\!OC \cdot CH_3
\end{array}
$$
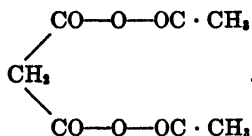
In a succeeding paper (23) the properties of these compounds were discussed. Carbon suboxide split water from anhydrous oxalic acid and gave the oxalic anhydride C_2O_3, which immediately decomposed into carbon dioxide and carbon monoxide.

$$O:C:C:C:O + (COOH)_2 \rightarrow CH_2(COOH)_2 + C_2O_3 \rightarrow CO_2 + CO$$
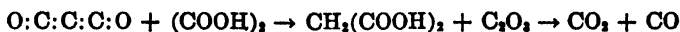
This reaction was carried out in acetone, and there also resulted the lactone of β-hydroxyisopropylmalonic acid.

$$
\begin{array}{c}
(CH_3)_2 : C\!-\!CH \cdot COOH \\
\qquad | \quad | \\
\qquad O\!-\!CO
\end{array}
$$
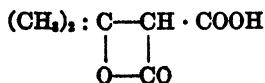
Malonic acid with carbon suboxide gave a product resembling polymerized carbon suboxide.

The reaction of carbon suboxide with hydrogen sulfide was

also studied (23).   With an excess of hydrogen sulfide the following reaction took place:

$$O:C:C:C:O + 2 H_2S \rightarrow H_2C(COSH)_2 \rightarrow COS + CH_2COSH$$

When both were in the proportion of one to one, colorless crystals were formed to which the constitution

$$
\begin{array}{c}
\text{CO—S—OC} \\
\diagup \qquad\qquad \diagdown \\
H_2C \qquad\qquad CH_2 \\
\diagdown \qquad\qquad \diagup \\
\text{CO—S—OC}
\end{array}
$$
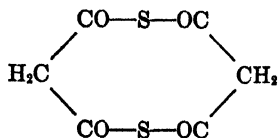
was assigned.

This substance reacted with ammonia according to the equation

$$
\begin{array}{c}
\text{CO—S—OC} \\
\diagup \qquad\qquad \diagdown \\
H_2C \qquad\qquad CH_2 \\
\diagdown \qquad\qquad \diagup \\
\text{CO—S—OC}
\end{array}
+ 4\ NH_3 \rightarrow 2\ H_2C
\begin{array}{c}
\diagup\ \text{COSNH}_4 \\
\diagdown\ \text{CONH}_2
\end{array}
$$
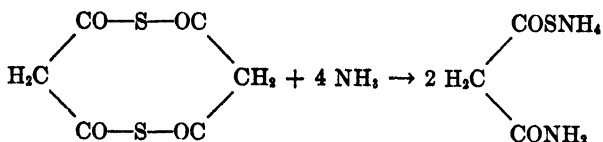
forming the ammonium salt of thiomalonamidic acid.   When heated in a high vacuum the substance decomposed.

$$
\begin{array}{c}
\text{CO — S—OC} \\
\diagup \qquad\qquad \diagdown \\
H_2C \qquad\qquad CH_2 \\
\diagdown \qquad\qquad \diagup \\
\text{CO—S—OC}
\end{array}
\rightarrow C_3O_2 + H_2C(COSH)_2 \rightarrow COS + CH_2COSH
$$
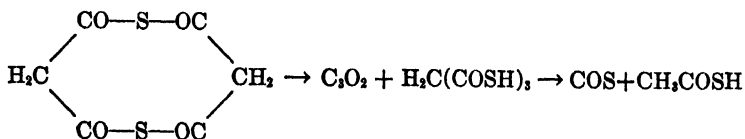
van Alphen (24) studied the action of ketenes, including carbon suboxide, on various hydrazine derivatives, such as phenylhydrazine, phenylhydrazine with substituents in the nucleus and methylhydrazine.   From the results with the ketenes, one would have expected from carbon suboxide and phenylhydrazine to obtain malonyl-bis-phenylhydrazide,

$$
\begin{array}{l}
\text{CO—NHNHC}_6H_5 \\
| \\
CH_2 \\
| \\
\text{CO—NHNHC}_6H_5
\end{array}
$$
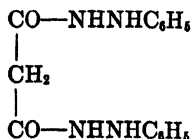
However this compound was not obtained. It is probable that phenylhydrazine reacted thus:

$$C_6H_5NHNH_2 + O:C:C:C:O \rightarrow C_6H_5NHNHCOCH:C:O$$

$$\downarrow I$$

C_6H_5—N————N   ←   C_6H_5—N————NH
  | ‖ | |
O : C—CH_2—C—OH   CO—CH_2—CO
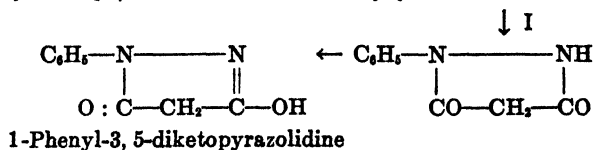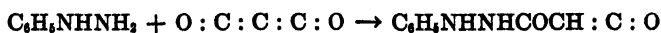
1-Phenyl-3, 5-diketopyrazolidine

III   II

Formula I was ruled out since the compound would not react with aniline to give the expected $C_6H_5NHNHCOCH_2CONHC_6H_5$. Compound II was easily changed to its tautomer (III) by heating or allowing to stand. On boiling with water the compound was split to phenylhydrazine and malonic acid. When there were two moles of phenylhydrazine to one of carbon suboxide a molecular compound of structure

C_6H_4—N————NH
  | | + C_6H_5NHNH_2
O : C—CH_2—C : O
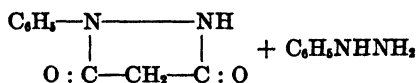
was formed. Similar compounds were formed using o-tolyl-, m-tolyl-, o-nitrophenyl-, p-nitrophenyl- and methyl-hydrazines.

With urea a small amount of barbituric acid was formed.

NH_2   C : O   NH—CO
  | ‖ | |
CO   +   C   →   CO   CH_2
  | ‖ | |
NH_2   C : O   NH—CO
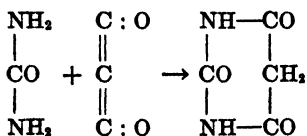
With p-phenylene diamine a white compound was obtained which was insoluble in all solvents and which had not melted at 320°. The constitution assigned to it is represented by either (A) or (B).

NH————CO   NH—COCH_2CO—NH
       |
      CH_2
       |
NH————CO   NH—COCH_2CO—NH
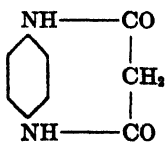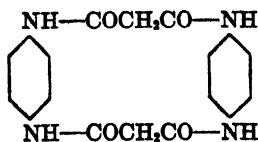
(A)   (B)

Similar compounds were formed with *m*- and *o*-phenylene diamine, and the structures (C) and (D) were assigned to these compounds.

(C)   (D)
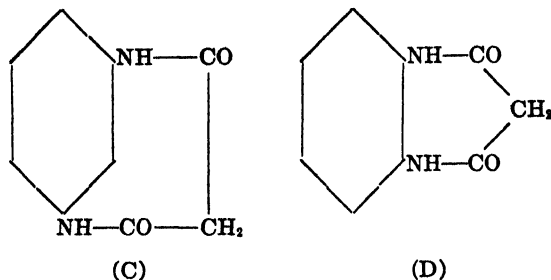
TABLE 1

Addition compounds formed by carbon suboxide and tertiary bases

	PROPORTION OF BASE TO C_3O_2
Isoquinoline...	1:1
Quinoline...	1:2
Quinaldine..	1:2
Nicotine..	1:3
Codeine..	1:5
Atropine...	1:5
Quinine..	1:7

Diels and Hansen (25) studied the reaction of carbon suboxide with sulfur dioxide and suggested the reaction

$$O:C:C:C:O + SO_2 \rightarrow CO_2 + O:C:C:S:O$$
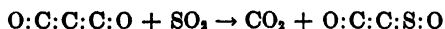
followed by the polymerization of the latter compound. They found that tertiary bases formed addition compounds with carbon suboxide and prepared a series of these compounds. (See table 1.)

POLYMERIZATION OF CARBON SUBOXIDE

The highly unsaturated character of carbon suboxide causes it to polymerize very readily. Diels and Wolf (5) found that the liquid at room temperature changed in the course of a day into a solid, amorphous, dark red substance which was completely

soluble in water giving a red-brown or eosin-red solution. At a higher temperature (37°) the polymer loses carbon dioxide, leaving a product which contains less oxygen and is but partially soluble in water. The action of heat on the polymerized carbon suboxide thus explains the series of oxycarbons observed by Brodie and by Berthelot. The polymer when heated gave off carbon dioxide, carbon monoxide, and also carbon suboxide in fairly considerable amounts. The residue even when heated to glowing was not carbon, but a carbon oxide very poor in oxygen (8). The polymer resembled the monomolecular form in its anhydride properties. It rapidly took up water from the air and dissolved in water with the simultaneous evolution of carbon dioxide.

Jones and Robinson (16) found that large quantities of a red solid having the properties of polymerized carbon suboxide were formed when they attempted to purify diamyl and diethyl thiomalonates.

Stock and Stoltzenberg (18) believed the polymerization to be decidedly autocatalytic. The speed of reaction depended upon the nature of the surface of the vessel. The presence of phosphorus pentoxide accelerated the polymerization extraordinarily. Ott and Schmidt (22) found that carbon suboxide prepared from diacetyltartaric anhydride did not polymerize over phosphorus pentoxide, and attribute the results of Stock and Stoltzenberg to traces of volatile phosphorus compounds in the carbon suboxide prepared from malonic acid and phosphorus pentoxide. They also reported keeping pure carbon suboxide in sealed glass tubes for a quarter of a year without polymerization. Diels, Beckmann and Tonnies (23) reported that this result was wrong and that the carbon suboxide prepared by this method polymerized with the same rapidity as that used in the earlier investigations.

Edwards and Williams (26) found that the oxide in the gaseous state was very stable, even at room temperature, when dry and contained in a glass vessel the surface of which had not been previously contaminated with the polymerized product. It could not be stored over mercury for any length of time or in the presence of moisture without the occurrence of polymerization. The

dried gas was not appreciably affected by exposure to ultra-violet light. The polymerization occurred on the surface of the containing vessel and the decrease in pressure was measured. The values of the velocity coefficient were calculated from the change in pressure on the assumption that from one to six molecules might be taking part in the reaction. The values so calculated fell off with the time, which led the authors to state that the reaction was probably a catalytic surface reaction.

The decomposition of carbon monoxide in the corona discharge due to alternating electric fields was carried out by Lunt and his coworkers (27), who studied the kinetics of the formation of the red polymer and its properties.

Some guesses have been made as to the probable structure of the polymerized carbon suboxide. Hartley (7) assigned to it the formula:

$$
\begin{array}{c}
C \\
O-C \quad\quad C-O \\
O-C \quad\quad C-O \\
C
\end{array}
$$
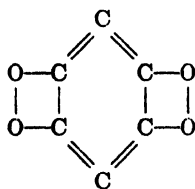
From its anhydride properties Diels, Beckmann and Tonnies (23) believe it to be:

$$
O{=}C{=}C \underset{CO}{\overset{CO}{\diagdown}} C \underset{CO}{\overset{CO}{\diagdown}} C \underset{CO}{\overset{CO}{\diagdown}} C{=}C{=}O
$$

X
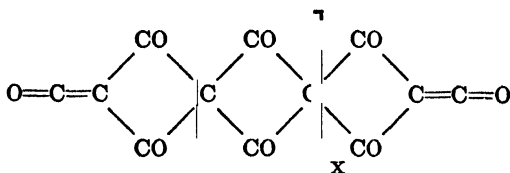
CARBON SUBSULFIDE

The sulfur analog of carbon suboxide was known long before carbon suboxide. It was prepared in 1893 by von Lengyel (28) who passed an electric arc through the vapors from boiling carbon disulfide and obtained a few grams of a deep red liquid whose composition corresponded to the formula C_3S_2. It was also

prepared by passing carbon disulfide vapors through a heated tube (29).

It is an oily, evil-smelling liquid at room temperature. It melts at $-0.5°$, but on heating it changes to a hard black mass; however, it can be distilled at 60° to 70° in a vacuum with but a small amount of polymerization.

von Lengyel named the compound tricarbonium disulfide. Stock and Praeterius (30) assigned to it the constitution $S:C:C:C:S$ and called it carbon subsulfide. They showed that it was similar to carbon suboxide in its chemical reactions, such as its reaction with aniline to form thiomalonanilide. Although more stable than carbon suboxide, it polymerized slowly at room temperature and in a few minutes at 100° to a black solid which was insoluble in water, sodium hydroxide solution and hydrochloric acid.

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A STUDY OF MERCAPTAN CHEMISTRY

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The study of sulfur compounds represents a relatively neglected page of organic chemistry. In at least two directions its importance is becoming felt more and more strongly,—the field of industry and the field of biochemical research. The recognition is rife that many raw products, such as petroleum, shale oil, tars, etc., contain a wide variety of sulfur compounds which imperatively demand removal and utilization. Equally pressing is the discovery that sulfur compounds play a prominent part in organic metabolism, where the —SH group achieves a fundamental rôle hitherto not fully realized.

We have chosen for discussion the more restricted field of mercaptan chemistry, using the old term "mercaptan" in the wider sense of any compound containing one or more —SH groups. Our objectives in this paper are: (1) a critical presentation of the accumulated data in this field, (2) a discussion of the results of such a presentation, and (3) the outlining of outstanding research problems that suggest themselves to active workers in this field.

We propose to treat the subject of mercaptan chemistry under the arbitrary but systematic headings of the following outline:

     I. Physical Characteristics
    II. Chemical Characteristics
   III. Method of Preparation and Purification
    IV. Detection and Determination
     V. Special Interest Attaching to the Substances
    VI. Research Problems

The subheadings will become apparent in the discussion. Our chief objective is to point out the essential facts and to indicate

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their continuity with the corresponding facts of better known analogous compounds, such as the alcohols, phenols, etc. At the same time novel features and unsolved problems are bound to come to light. An effort, therefore, will be made to present speculative discussion right on the heels of the facts, with the hope of at least raising questions even if no final answer can be given.

I. PHYSICAL CHARACTERISTICS

1. General appearance

Physical state. Methyl mercaptan (1) appears to be the only normally gaseous member of the type RSH, where R is substantially any type of radical. Hydroxymethyl mercaptan (2), however, is a solid. The aliphatic mercaptans, in so far as they have been prepared, are liquids. Yet, β-aminoethyl mercaptan (3) is a solid. It may be surmised that substitution of groups in the molecule has quite a marked effect on the physical state.

Comparing mercaptans with corresponding oxygen compounds in regard to physical state reveals some differences. There are no gaseous members in the oxygen series. In the sulfur series thiophenol, *o*-thiocresol and α-naphthyl mercaptan are liquid (4); in the oxygen series the corresponding compounds are solid. *p*-Thiocresol and *p*-cresol, however, are both solids (5). The trend, of course, is more distinctly brought out in the data on melting points and boiling points.

Crystal structure. There is a general dearth of data in this field, though vague descriptions abound in which reference is made to "needles," "leaflets" or "platelets." Where a series of compounds has been observed, e.g. the thiosulfocarbamates, NH$=$C(SH)SR (6), there is no consistency or continuity in crystal structure among homologues. Studies of the simpler members of the aliphatic series should be of interest, but are still unavailable.

Color. Aliphatic mercaptans are almost exclusively colorless. This is so consistently true that any description of a preparation as "yellowish" would throw doubt on its purity. Thiophenol, the thiocresols and the naphthyl mercaptans (4, 7) are colorless,

and it is possible that other members of the aromatic group are not as yellow as they have been reported to be. On the other hand, it is quite evident that in a case like that of p-acetaminothiophenol, two varieties may exist, one colorless and the other yellow (8). The colorless variety would be

NHCOCH₃

and the yellow,

Phenyl β, β'-dimercaptovinyl ketone,

$$C_6H_5COCH : C(SH)_2,$$
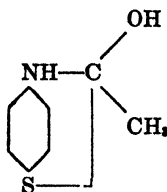
gold yellow platelets, may also be a case similar to that of p-acetaminothiophenol, although the existence of two forms has not been noted (9). Heterocyclic types furnish us with cases where a decided color may be expected. Thus, phentriazoxine mercaptan
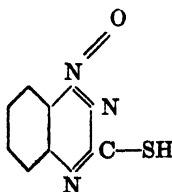
forms red needles (10). o-Quinolyl mercaptan (11) is also red.

More complex forms, as α-mercapto-β-carbethoxythio-γ-pyrone-β_1- hydroxythiophene, show different crystal forms of different color, as orange-red prisms and yellow needles, depending on

possible internal rearrangements (12). In any case the rôle of an —SH group in conferring color properties is apparently very similar to that of an —OH group (13). We should like to suggest that a close examination of the question would reveal that contamination with disulfides may have led to erroneous observations on color in quite a few cases, and that more analogies with hydroxy compounds will be borne out as undue complicating factors of complexities of structure are ruled out.

Odor. The unpleasantness of the odor of the mercaptans is proverbial. The odors have been referred to as "evil," "provoking," "unbearable," "furchtbar," and the like. It is hard to see how one observer specifies thiophenol as having a garlicky, but "not unpleasant" odor (7a); but *de gustibus non est disputandum.* Nonyl and decyl mercaptans rise almost to the status of perfumes. Decamethylene thioglycol has been approved (14). *p*-Phenylene dimercaptan has a "peculiar odor" (15), while β-thioanthrol, myricyl mercaptan, *o*-quinolyl mercaptan and *o*-xylylene dimercaptan are completely odorless (16, 16a, 16b, 16c). The parallelism with hydroxy compounds is evident in spite of prejudice. It is possible, we have noted, to detect the choking effect of the butyl and amyl alcohols in the corresponding mercaptans. In some cases curious cancellations occur, as in pyridine mercaptan, which is almost odorless (17). There is some evidence that marked odor changes may be due to tautomerism. We may expect an equilibrium between
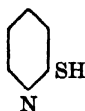
and
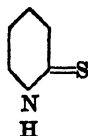
the latter yielding derivatives of ferocious odor. Should some such considerations rule this field there may be in it a rich har-

vest for the "Riechstoff" chemist, and, perhaps, the psychologist as well.

Taste. Either unusual courage or accident has produced the observations that *o*-quinolyl mercaptan,
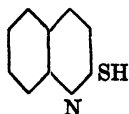
is tasteless and
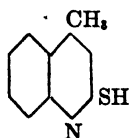
is bitter (16b). Myricyl mercaptan is also tasteless (16a). Thioglucose has a sweet but unpleasant taste (18). Since these compounds have no characteristic odor, they may perhaps find some use for abnormally jaded appetites.

Miscellaneous. A direct, fast, orange dye is available in *o*-quinolyl mercaptan (16b).

2. Identifying constants

Density. The density data reported are of no high order of reliability. For aliphatic mercaptans they merely indicate a range of 0.833–0.894 without any consistent regularity, probably due to experimental error. The aromatic mercaptans are in general heavier than water. The thioglycols are also heavier (19). This is in general agreement with hydroxy compounds.

Thermal constants. (*a*) *Boiling points and melting points.* The usual chaos of data exists with regard to melting and boiling points. Thus, ethyl mercaptan is reported to melt at −121°C. as well as at −144° (20). It may be suggested that hydrate formation is probably a factor in some cases. An interesting instance is that of *o*-quinolyl mercaptan with two molecules of water of crystallization. It melts at 58–9°, and in a desiccator gradually changes to a violet liquid (11). The hydrate is solid, the anhydrous compound is liquid.

The boiling points of mercaptans are generally consistently lower than those of the corresponding alcohols or phenols or glycols. A convergence becomes apparent for higher homologues

TABLE 1

Comparison of the boiling points of some mercaptans with those of the corresponding hydroxy compounds

RADICAL ATTACHED TO THE -SH OR -OH GROUPS	MERCAPTAN	HYDROXY COMPOUND
	Boiling point in °C.	*Boiling point in °C.*
Methyl (21)	5 8–7 6	66
Ethyl (22)	34.7–37	78.4
n-Propyl (23, 22a)	65 –68	97.4
Isopropyl (22a)	53 –59	82 8
n-Butyl (24, 23, 22a, 21)	96 –98	117
Isobutyl (22, 22a)	86.6–88	106.5
Isoamyl (25, 22)	116.6–122	130
n-Hexyl (26, 22a, 21)	145 –8	157
n-Heptyl (22a, 21)	174 –5	175 8
Ethylene (27)	146	197–197.5
β-Phenylethyl (28)	105 at 23 mm.	212
γ-Phenylpropyl (28)	109 at 10 mm.	235 or 119 at 12 mm.
Propylene (19)	152	188
Trimethylene (19)	169	214, 227
Allyl (29)	90	96.6
Phenyl (30, 5)	166 –170	182.6
Tolyl (in *o* position) (5)	194 –195	190 8
Tolyl (in *p* position) (31)	190.2–191.7	201 8
Benzyl (32)	165, 194–5	204.7
m-Xylylene (33)	157–8 at 15 mm.	⎧1, 3, 2........211.2 ⎨1, 3, 4........211.5 ⎩1, 3, 5........219.5
Naphthyl (-SH or -OH in position 1) (5)	285	278–80
Naphthyl (-SH or -OH in position 2) (34, 7)	153–4 at 15 mm. 286 at 760 mm.	285–6
Furfuryl (-SH or -OH in position 2) (35)	155	168–70

where the effects of other groups predominate. The few instances given in table 1 will suffice to show this. The curves in figure 1 give a comparison of the boiling points of some mercaptans with those of the corresponding hydroxy compounds.

It is our opinion that the differences are not to be explained merely on the basis of different degrees of association, since in some cases the values of the two series are too close and in a few instances the relations are actually reversed.
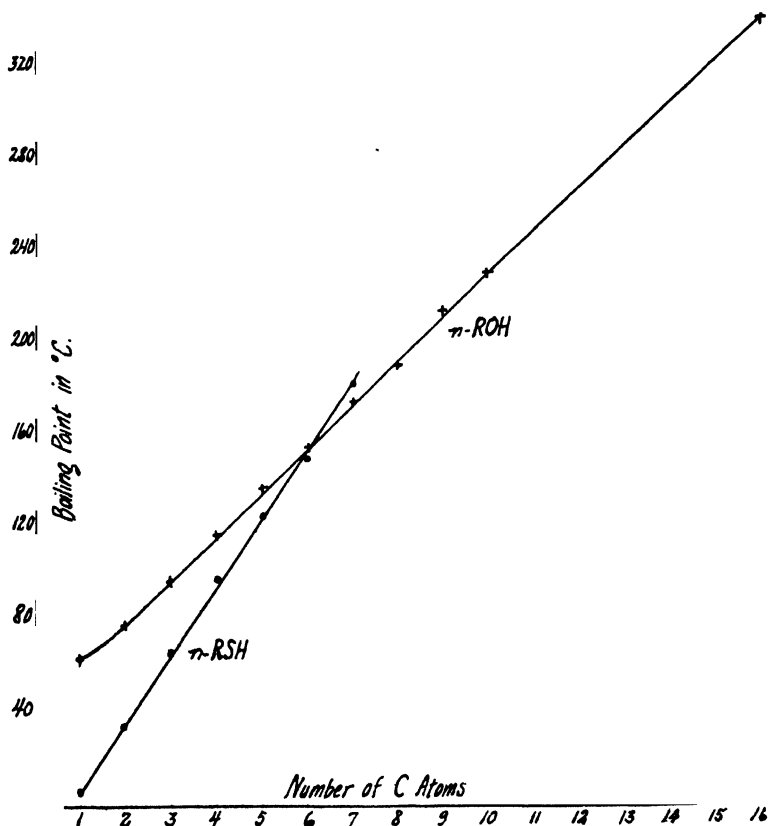
FIG. 1. BOILING POINTS OF SOME MERCAPTANS AND OF THE CORRESPONDING HYDROXY COMPOUNDS

(b) *Heats of combustion and of formation.* This is a promising but much neglected field. Several measurements have been made. Reference can be made (36) particularly to some experiments and calculations tending to show that the secondary val-

ences of sulfur in RSH are much less than those of oxygen in ROH (alcohols). The procedure involved the measurement of the heats of formation of the addition compounds formed by the given compound and the Grignard reagent, ROMgI. These results were checked by displacement of the sulfur compounds by the corresponding oxygen compounds. The heat of formation of the sulfur compounds and the heat of displacement by the oxygen compounds together equal the heat of formation of the oxygen addition compounds. In this way, the secondary valences of sulphur and oxygen are compared. The explanation is probably connected with the gradual increase in basicity as we go through the series sulfur, oxygen and nitrogen.

(c) *Other thermal data.* Other thermal data, as specific heats, latent heats and the like, seem to be entirely lacking. There are a few isolated measurements on the variation of vapor tension with temperature (37) and a few determinations of critical temperatures (38, 22c, 22d), the latter being somewhat lower than for oxygen compounds. Ethyl mercaptan has been reported as forming mixtures of minimum boiling point with *n*-pentane and trimethylethylene (39). A harvest of analogies, involving matters coming in contact with theoretical issues, is quite certain to be discovered in this field.

Optical constants. Refractive indices have been obtained for only a few mercaptans (40, 22, 19a, 5). These yield a value of 7.76 for the atomic refraction of sulfur (21), thus checking results on other sulfur compounds. Estimates have been made on very limited data of the optical exaltation of the grouping

$$C=\!\!\!=C-SH \quad (30b)$$
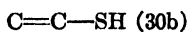
Optically active amyl mercaptan has been studied slightly (41), and mutarotation has been observed for glucothiose (42). Absorption spectra of phenol and thiophenol have been compared (43). In spectra of the vapor the chief contrast is a shift from some 70 bands for phenol to 2 weak bands for thiophenol at 2870 and 2798. On the basis of such facts it would be difficult to

develop any method of detection of thiophenol in phenol, but probably phenol in thiophenol would be easily noted. Many interesting possibilities come to mind which would have theoretical as well as practical utility, but there is still very little to be gathered from the scanty observations except that both positive and negative analogies must be plentiful.
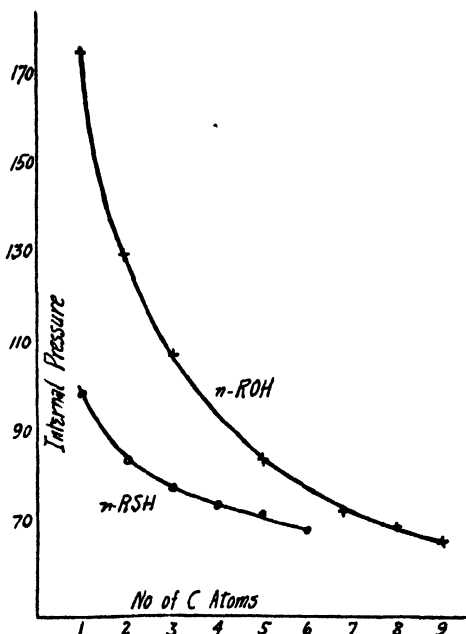
Fig. 2. Internal Pressure of Some Mercaptans and of the Corresponding Hydroxy Compounds

Electrical constants. Measurements of conductivity are available in some cases for thio acids, showing an increasing acidity on the replacement of sulfur for oxygen (44). It is taken for granted that mercaptans are more acidic than alcohols and phenols, but it is not known how much more acidic they are on the basis of conductivity or just where they stand in mutual relation. Furthermore, the effect of substituting groups may be quite different in the sulfur series as compared with the oxygen series. There is no *a priori* reason for assuming additivity effects.

Miscellaneous constants. We have charted a series of values for the internal pressure of mercaptans (see figure 2) comparing them with the alcohols, according to the empirical formula:

$$\text{Internal Pressure} = \frac{5200 + 30\ T}{\text{Molecular Weight}} \times \text{Density at } 20°C.,$$

where T is the boiling point in °C. (45).

To complete our list we will mention some isolated viscosity measurements (46, 19a). Ethyl mercaptan shows higher values than ethyl alcohol, but mixtures of the two give still higher values. The "adhesional work" between ethyl mercaptan and water has been measured (47). It is less than that for ethyl alcohol. An internal pressure of 1490 atmospheres is reported, and γ_σ in the Ramsay-Shields formula is 18.95 (48). These results may be of some value in the study of solubility. Fragmentary data on cryoscopic behavior of phenyl mercaptan in phenol are also reported (49).

3. Distribution data

Solubility in various solvents. In the matter of solubility considerable contrasts are to be found between mercaptans and alcohols and phenols. The aliphatic mercaptans are insoluble in water except for such compounds as hydroxymethyl mercaptan (2) and β-aminoethyl mercaptan (3) which have solubilizing groups. Ethyl mercaptan at the same time forms a crystalline hydrate below 8° (50). The matter, however, is complicated by contradictions among observers. Thus, monothioethylene glycol is reported as slightly soluble (51), and also as completely miscible (51a, 19a). The contrasts between sulfur and oxygen types, however, are more likely. Compare for instance, the fact that *p*-nitrothiophenol is easily soluble in water (52), with the fact that *p*-nitrophenol is soluble only with difficulty.

In alcohol the solubilities of most simple mercaptans are consistently high. Moderate solubility is shown by triphenylmethyl mercaptan (53). More complex types, such as phentriazoxine mercaptan (10) and β-thioanthrol (16), are difficultly soluble. This contrasts again with the very high solubility of triphenylcarbinol and of β-anthrol in alcohol.

A further contrast in solubility is found in the fact that β-thioanthrol is not very soluble in ether, whereas β-anthrol is. Triphenylmethyl mercaptan (53) is only moderately soluble in ether, the corresponding carbinol being very soluble. Otherwise ether is an excellent solvent for mercaptans as well as for alcohols and phenols. The same apparently applies to benzene, and probably, to judge from scanty data, to carbon disulfide and chlorinated solvents.

A phenomenon of color change on solution is to be found in the case of ana-bromo-o-quinolyl mercaptan (11), yellow in the solid state and reddish in acetone. This resembles the color change often noted in the case of disulfides. This factor is here eliminated because the disulfide is white. It is probable that more such cases will be discovered and that their explanation would point to some form of association with the solvent.

Adsorption, diffusion, partition, etc. No quantitative data have been published in the literature, though patents abound on the adsorption of mercaptans by metallic sulfides (54). In particular the activity of cupric sulfide is receiving some attention at present.

Partition studies are scarce. The distribution between hydrocarbon solvents and various strengths of caustic soda, at least for the aliphatic series (55), has been taken up on account of the commercial urgency of the issue. The mercaptans are very weak acids indeed, and are largely inextractable and become totally inextractable as the molecular weight increases. A curious datum is the reported solubility of *secondary* hexyl mercaptan in potassium hydroxide of specific gravity 1.22 and its separation into two layers at higher temperatures (56). This may be due, however, to increased hydrolysis of the potassium mercaptide formed, and not to any pure distribution phenomenon.

To summarize the state of our knowledge as to the physical characteristics of mercaptans, we should like to point out that the field is a fertile one for further study. There is a total, or almost total, lack of data on dielectric constants, conductivity, internal pressure, vapor tension, thermal constants necessary for thermodynamic calculation, and optical measurements. Many cor-

rections of the available data are needed. Distribution data in particular require re-working on a quantitative basis.

II. CHEMICAL CHARACTERISTICS

1. Stability and decomposition

Thermal. Little has been done along the lines of a detailed systematic study of the thermal stability of mercaptans. The evolution of hydrogen sulfide has been noted, and the formation of other products more or less guessed at (57, 51, 16). Therefore, we find both sulfides and disulfides and even elementary sulfur referred to. Then again catalysts seem to affect the reaction markedly (58). As to the decomposition of metal derivatives of mercaptans there is also disagreement. In the case of lead and similar mercaptides some authors write reactions showing only sulfide formation; others include the formation of some free mercaptan (59, 23, 7). There is also no doubt that mild decomposition sets in even under conditions of steam distillation in many cases, especially with the higher aliphatic members (60, 22a).

More should be done to segregate stable types from unstable ones. Thus thio acids, carbithionic acids (571) and complex mercaptans belong to the latter group. Particularly unstable are the mono-, di- and tri-thioglycerols, hydrogen sulfide being given off even below 100°. Triphenylmethyl mercaptan also shows ready decomposition. Occasionally a very special case turns up, such as that of 2,4,6,-trinitrothiophenol which explodes similarly to picric acid (57d).

As a matter of fact—and our own unpublished work supports it strongly—by analogy with the alcohols one should expect olefin formation along with hydrogen sulfide, and, in the presence of some specific catalysts, hydrogen formation along with thio aldehydes. This has been surmised also by Hurd (61) who formulates the possible reactions:

$$CH_2{=}CH_2 + H_2S$$

$$CH_3CH_2SH$$

$$[CH_3{-}CH{=}S] + H_2$$
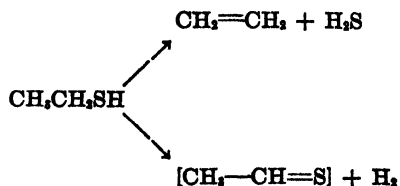
The thioacetaldehyde, he speculates, may form tetraphenylthiophene. We have not found this latter speculation to be true. In general, olefin formation for the aliphatic types is predominant, and stability decreases with increasing molecular weight. The aromatic types are less stable than the aliphatic and probably follow a different course of reaction.

Electrical decomposition and dissociation. No direct data are available. A few electrolytic oxidations, limited to thiourea types in which disulfides are formed, would indicate the existence of an anion due to slight dissociation as acids (62).

Photochemical decompositions. No data were found concerning photochemical decompositions.

Miscellaneous:—tautomerism, rearrangements. In the study of the stability of compounds containing the —SH group one must keep in mind the possibilities of tautomerism and rearrangement. We may cite the case of thiocarbanilide (63), the ordinary formula of which is

$$S = C(NHC_6H_5)_2,$$

but which behaves with halogen alkyls as if it were

$$C(=NC_6H_5)(SH)(NHC_6H_5).$$
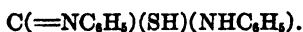
This is general for the group

$$—C—NH$$
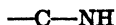
as in thiourethans, thiosemicarbazide, etc. (64).

Very similar is the reported tautomerism of thioacetamide caused by iodine (65). Cases more removed from these types are illustrated by the rearrangement (3) of β-mercaptoethylphthalimide to β-mercaptoethylphthalamic anhydride:

$$\diagdown NCH_2CH_2SH \rightleftarrows$$

$$\begin{array}{c} \cdot NH—CH_2 \\ \diagup CO—S—CH_2 \end{array}$$
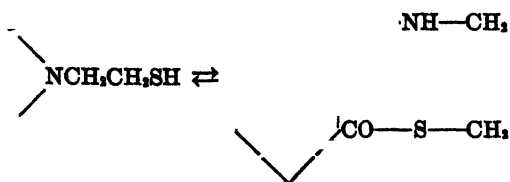
p-Acetaminothiophenol also shows two forms, one yellow and stable, the other colorless and labile (8).

A type of change recently discussed is the equilibrium between esters of dithiocarboxylic acids and pseudo acids (44):

$$RC(: S)S \cdot C_nH_{2n+1} \rightleftarrows RC(: S)SH$$

These pseudo acids form pseudo salts.

Similar considerations apply to perthiocyanic acid which may be pictured in two forms (66):

Pseudo form   Labile form
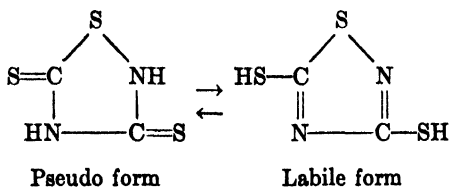
The —SH group also gives rise on occasion to the so-called "thionylium ring" (67), as illustrated by aromatic *o*-hydroxy-sulfides:

Isosulfide   Dehydrosulfide
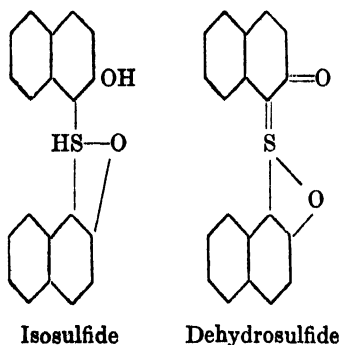
In this connection we should like to point out that such studies are very likely to assume an important rôle in the investigation of the biological equilibrium of complex organic compounds containing an —SH group. Dextro and levo isomers of mercaptans and their Walden inversion are already attracting some attention (68).

2. Formation of addition compounds

A crystalline hydrate of ethyl mercaptan has been reported (50). There seems to be no reason why other mercaptans should not form hydrates also. Some parallelism, too, may be found in the consideration that mercaptides often form hydrates (69). Nevertheless, the possibility, suggested by analogy, of the addition of hydrogen sulfide instead of water has apparently not been tested.

Unsaturated hydrocarbons form addition products. Phenyl and benzyl mercaptans add to styrene, 1,1-phenylmethylethylene, trimethylethylene and some terpenes (70). When compounds like benzylidene benzoyl acetone or cinnamylidene acetophenone, representing a very large variety of unsaturated ketones and diketones, are found to add mercaptans it is due, no doubt, to their functioning as unsaturated hydrocarbons (71). In conformity with expectation in such cases the mercaptan residue adds to the most hydrogenated carbon atom.

Addition reactions have been reported for halogenated hydrocarbons with mercaptans of the type of o-quinolyl mercaptan and the so-called thio amides (72). It is interesting to note that the same types form double salts with mercury, platinum, zinc and lead halides (73, 16b). This suggests a probability that similar cases would be forthcoming amongst mercaptans containing heterocyclic rings, e.g. imidazole mercaptan and its derivatives. Perhaps we may include in this set "chloral phenyl mercaptan," which is a definite individual, and a series of addition compounds formed preliminary to condensation between chloral and monothioethylene glycol or halogenated aromatic mercaptans (74).

A reaction quite analogous to the addition of aldime (HCl· HCN) to phenols and phenol ethers is brought out in the case of all mercaptans, including the aliphatic types (75). Iminothioether hydrochlorides are formed. The addition is of even wider significance, since in the presence of hydrogen chloride the place of hydrogen cyanide can be taken by acetonitrile, phenyl nitrile, benzyl nitrile, trichloroacetonitrile, and phenylene dinitrile (76).

Additions with various quinones, phenanthraquinone and chrysoquinone have been found, in particular for *n*-butyl, amyl, benzyl and phenyl mercaptans (77). This is analogous to the addition of phenols to quinone. We should also expect, therefore, similar reactions for polymercaptans, since the reaction occurs for polyphenols.

Observations have also been made on the addition of unsaturated acids, such as acrylic and cinnamic acids, and ketonic acids, such as pyroracemic acid, to aromatic mercaptans (74a). There are, however, quite a few irregularities and exceptions which in themselves should prove interesting. Both aromatic and aliphatic mercaptans seem to add to isatin and its derivatives. Compounds with ethylene oxide have been found (79). A group of mercaptans of the type of β-aminoethyl and β-methylaminoethyl mercaptans, are characterized by picrate formation (3). An odd case is the formation of an addition compound of ethyl mercaptan with the methyl ester of azodicarboxylic acid (80). All these, of course, do not by any means exhaust the possibilities (81, 63, 57b).

It may be said that on the whole both the aliphatic and aromatic mercaptans come closer to phenols in respect to addition compound formation than to aliphatic alcohols. We are also of the opinion that the separation and study of addition types is likely to be simpler in the case of sulfur compounds than in that of oxygen compounds. As an instance we might cite the case of benzyl mercaptan adding to benzaldehyde to form benzyl α-hydroxybenzyl sulfide in the absence of a condensing agent (81), a case in which a clean cut distinction can be made between addition and condensation.

3. Condensations

With compounds containing aldehyde and ketone groups. Numerous condensations have been reported with aldehydes (82, 78d, 74, 57j, 33), ketones (83, 82g, 78d, 77, 62a), ketonic acids (78), sugars (84, 41), aldehydes in conjunction with bases, and the like. In the synthesis of soporifics, mercaptals, formed from aldehydes, and mercaptoles, formed from ketones, have played

an important part. A very strange contrast is that the analogues of the mercaptoles cannot be made by the same procedure in the alcohol series. Mercaptals have been made from aliphatic mercaptans and dimercaptans with many aromatic aldehydes, and even cyclic aldehydes such as thienyl acetaldehyde (82g). Aromatic mercaptans have been condensed with both aliphatic and aromatic aldehydes in a wide variety of combinations. Piperonal, cinnamic aldehyde, and furfural (78d) appear in a long list of reagents, and the mercaptan proper reactions have been extended to aliphatic thio acids. The last mentioned form dithioaldehyde aliphatic acids, which show a structure analogous to that of the mercaptals. Thus, dithiobenzaldehyde acetic acid would be $(C_6H_5)CH(SCH_2COOH)_2$. Few reactions with formaldehyde have been tried (82e, 82i, 82k). Keeping in mind the complications that arise in the reaction of phenols with formaldehyde, it would be of interest to see the matter investigated. One would expect, for instance, to find the sulfur analogues of $HO(C_6H_4)CH_2(C_6H_4)OH$, and $HOC_6H_4CH_2OH$, which are formed under different conditions in the reaction of phenol and formaldehyde.

Amongst the ketones used in condensations we find acetylacetone (83a), thiophenylacetone (83), thioethylacetone (83), 2, 3-diphenylindone (77), and diketones of the type XCOYCOZ (83a) in combination with aliphatic and aromatic mercaptans, including thio acids and derived forms as, for example, β-ethoxyethyl mercaptan (83b).

α-Ketonic acids show similar behavior readily; β-ketonic acids less readily. Thioglycolic acid condenses readily with acetoacetic ester. The data are scarce but many extensions ought to be possible (78).

Condensations with sugars are receiving a great deal of attention. Thus methyl mercaptan and grape sugar will condense to glucose methyl mercaptal, $CH_2OH(CHOH)_4CH(SCH_3)_2$. This may go over to an alkyl glucoside. Arabinose, galactose, mannose, rhamnose, xylose, lactose, rhodeose, fucose, and many others and their derivatives figure in these syntheses.

Esterification. Esterifications have been accomplished directly

in many cases.   Thus methyl mercaptan and formic acid form a
methyl trithioester.   It is not imperative to use methyl formate
or formamide or chloroform in the presence of alkali, though such
methods are also operable.   This applies to both aliphatic and
aromatic types (85, 82b).   Both mono- and di-acetyl compounds
are reported (85c, 85d, 85e, 85f, 85g, 57k, 34, 15).   Occasionally
an esterification fails, as e.g. that of allyl mercaptan with formic
acid, but it is because of the instability of the mercaptan (82l).
An esterification with an inorganic acid, hydrochloric acid, is
reported only for triphenylmethyl mercaptan, with the evolu-
tion of hydrogen sulfide (53).   This would be expected by ana-
logy.   An interesting case is another such esterification of mono-
thioethylene glycol with concentrated hydrochloric acid (19a).
In this·experiment the alcohol group was esterified and the mer-
captan group remained unchanged.   This may not be a true basis
for comparing the competition between the $-SH$ and $-OH$ groups,
since the residual groups are not the same.   The analogies under
more comparable conditions have been tested, the limits follow-
ing in general the relations observed with alcohols, though much
lower.   The stability of esters decreases with increase in molecu-
lar weight (85h, 57k, 24a).   The failure of mono esters to turn
up in the case of formic acid is of particular interest, but it may
be merely a matter of conditions.   Furthermore, certain reactions
of phenols which one may come across in attempts to esterify, as,
for instance, with phthalic anhydride, to form either phthaleins,
and α-hydroxyanthraquinone, or the $AlCl_3$ condensation product,
$HOC_6H_4COC_6H_4COOH$, have not produced their analogues as
yet.   The formation of β-mercaptopropyl phthalimide from β-
aminopropyl mercaptan and phthalic anhydride indicates possi-
bilities in this direction (86).   It may also be noted here that
reactions between some alcohols and some mercaptans to form
sulfides, which are reversible, have also been considered as es-
terifications, i.e. the mercaptan may be treated as an acid.   Thus
benzyl alcohol reacts reversibly with ethyl mercaptan forming
the sulfide.   On the other hand, benzyl mercaptan reacts irre-
versibly with ethyl alcohol to form the ether (87).   Thus, too,
one may look upon condensations of mercaptans with aniline

to anilides (9) as another instance of esterification with the mercaptan in the rôle of an acid.

Reimer-Tiemann types. Condensations depending on the use of chloroform or carbon tetrachloride along with alkali have been worked out in some detail (88a). There is some analogy with alcohols and phenols. Thus mercapto acids may be made in the same way as hydroxy acids. Yet there may be some differences in orientation, and complications certainly do arise on account of ready disulfide formation from mercaptans or mercapto acids. Nor is the formation of salicylaldehyde from phenol paralleled with thiophenol, in which case an orthoformic ester is formed. The points of difference do illuminate the special problems of poor yields with oxygen compounds, pointing to explanations based on analogies to the sulfur compounds, rather than *vice versa.*

Ester exchange. By ester exchange we mean a condensation reaction in which substantially an esterification is accomplished by another ester (59a). This is illustrated by the equation.

$$RSH + R'ONO = RSNO + R'OH$$

Mercaptans react with organic nitrites to give a thionitrite and an alcohol or phenol (89). Even substituted mercaptans show this reaction, which we may guess is probably reversible, furnishing us directly with the oxygen analogue.

Somewhat similar are the reactions (90) characterized by the equation

$$M(SR)_2 + n\ NO \rightarrow (NO)_{n-1}MSR + NOSR$$
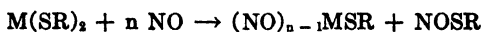
in which M = Ni, Co, or Fe. For Fe and Co, n = 3; for Ni, n = 2. Besides the esterification there is the formation of a curious metallic derivative.

Condensations with acid chlorides and the like. Reactions with chlorides of inorganic acids parallel the oxygen types. Yet phosphorus pentachloride, for instance, when reacting with a mercaptan may form a sulfochloride in addition to an ester (91). NOCl reacts to form thionitrites (59a). Phosgene (92), or thiophosgene (92a, 92b), and esters of chlorocarbonic acid (93)

condense normally. Polysulfide types may be obtained by the use of phosphorus sulfochloride (94), thus

$$3\ RSH + PSCl_4 \rightarrow PS(SR)_3 + 3\ HCl$$
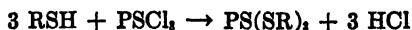
In the case of organic acid chlorides in conjunction with alkali we have numerous analogues of the Schotten-Baumann reaction. We have illustrations from among the simplest up to the most complex mercaptans. Other than sodium salts of the mercaptans may be used. Occasionally the matter is complicated by ring closure (72), as in the case of β-mercaptoisopropyl amine forming 4-methyl-2-phenyl-thiazoline when condensation with benzoyl chloride is attempted. Oxalyl choride has been used in a number of cases (96). Picryl chloride also leads to complications due to ring closure with the reagent (85e). A peculiar case is found in the reaction with o-hydroxythiophenol in which "phenoxthin," or 1,3-dinitrophenothioxin, is formed (97a), thus
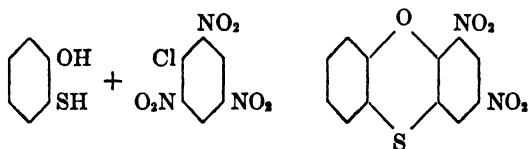
Further cases are too numerous to discuss (97, 85d, 82e, 82h, 74b, 59h, 57b, 57g, 50, 33, 28, 27, 14, 11, 7).

Types related to Williamson's reaction. The formation of sulfides analogously to ethers from organic halides and sodium mercaptides has been investigated for a large variety of compounds (98, 97c, 97e, 97n, 85c, 85d, 85e, 82c, 82g, 82h, 81b, 73, 33, 10, 9, 7, 3, 1). The reactions are not limited to sodium mercaptides. A frequent variant is found in the use of sodium ethoxide with the mercaptan and halogen derivative. It may be noted here that in some cases a complication may arise in that a sodium mercaptide will react directly with a mercaptan to form a sulfide, as seems to be the case in the reaction of cyclopentyl mercaptan and sodium ethyl mercaptide. This would lead one to expect analogies in the case of alcohols and phenols which remain to be discovered.

The halogen derivatives which may be used include chloroalkyl sulfides (97h, 82h) and sulfoxides (97h), chloroanthraquinones (97d), chlorohydrins (98x, 97n, 82c), and even chloromercaptides (98d), e.g. $C_6H_4(NO_2)SCl$. In the interesting case of condensation with $(SCN)_2$ and $RS-SCN$, the SCN group shows behavior analogous to that of the halogen (98b, 98t). Thus o-nitrophenol with $NCS-SCN$ yields $C_6H_4(NO_2)S\cdot SCN$ with the liberation of HSCN. β-Naphthyl mercaptan and $C_2H_5S\cdot SCN$ yield HSCN and $(C_{10}H_7)S\cdot SC_2H_5$. These products may condense further with more mercaptan giving disulfides of higher molecular weight. Cyanogen iodide (11), somewhat analogously, will convert an $-SH$ group to an $-SCN$ group. On the whole, there is also no reason for not including amongst such condensations reactions with alkyl sulfates (98s, 85d, 85e, 73, 10), with sulfonic acids and esters (100e, 98r, 98v, 97c, 81b, 15) and with rarer reagents, such as benzyl nitrate (98p). All of these have been tried to some extent.

Reactions with aryldiazonium salts, etc. Attempts have been made to parallel the action of phenols on diazonium compounds to form azo compounds. Aromatic mercaptans react with diazonium compounds to form diazothiophenol ethers which are converted readily to sulfides (99, 87). Disulfides are found as by-products and, in the not unusual contingency of an explosion, as the main products. There is a distinct contrast in these observations which deserves a great deal more attention.

Reactions with chloro acids, etc. Sulfide formation is the essential background of condensations with chloro acids, which resemble those given above for other chlorine-containing compounds (100, 98c, 97, 97j, 97k, 85e, 82j, 59h, 3). Esters of the chloro acids apparently do as well (100d, 93). To complete our list we would mention chloro- and bromo-ketones and an instance where diiododiethyl sulfone reacted analogously. Of more interest are the deviations from these standard forms, such as, for example, the reaction of benzyl mercaptan with ethylene dichloride and alcoholic alkali. Surprisingly, the *unsaturated* BzSCH $=$CHSBz is formed, as if there were a momentary formation of acetylene (98c). Curious also is the inversion that may occur with par-

ticular mercaptans possessing unusual characteristics. An instance arises in the condensation of β-aminoethyl mercaptan with ethylene chlorohydrin in which the hydroxyl group, rather than the chlorine atom, reacts with the hydrogen of the $-SH$ group forming $NH_2CH_2CH_2S \cdot CH_2 \cdot CH_2Cl$. In all other cases observed chlorohydrin reacts by way of the chlorine atom.

That sodium bisulfite may be split out in a condensation is illustrated by the combination of sodium anthraquinone sulfonates with mercaptans in the presence of alkali to form alkylmercaptoanthraquinones (100e, 100g). An entirely similar splitting out of KNO_2 occurs when nitroanthraquinone is treated with a potassium mercaptide (100f). We know of no analogous reactions in the oxygen series.

Ring closures. Several examples exist of aromatic mercaptans which on treatment with alkali form heterocyclic compounds (101, 97a, 86, 72, 57k, 27, 9). Such is *o*-(γ-chloropropyl)-thiophenol which forms $\alpha\beta$-benzopentamethylene sulfide or "thiochroman" (101d).

Otherwise one may rely on more or less standard procedures. Thio amides and ethylene dibromide (101a, 101b, 72) dithioethylene glycol and benzal chloride or ethylene dibromide (101e, 9), will yield ring structures. *o*-Aminophenyl mercaptans and nitrous acid go to diazo sulfides (101),

$$(C_6H_4)-N=\!\!=\!\!N$$
$$\diagdown\;\diagup$$
$$S$$
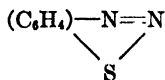
In this group we may also place the conversion of phenyl mercaptan to thianthrene
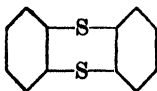
in the presence of aluminium chloride (101c). Again analogy proves to be a safe guide.

4. Oxidations

Oxidations by concentrated sulfuric acid, nitric acid, and the like. That the first step in the oxidation of mercaptans is disulfide formation and the last step sulfonic acid formation is well known. Yet the probable existence of sulfoxides and sulfones as intermediate products is quite usually ignored. Concentrated sulfuric acid and even sulfur trioxide are reported to form disulfides only (97e, 59, 5), yet evidence is available that other products are also present, e.g. phenyl mercaptan yields thianthrene and possibly diphenylene-*p*-disulfide and compounds responsible for a blue color (103). There is hardly any doubt that there is further action beyond simple disulfide formation, characterized by ring closures and polymerization (103, 101c). Our own work clearly indicates a similar situation for aliphatic types as well. In fact, it is possible to obtain parallel results with aluminium chloride, zinc chloride or phosphorus pentoxide once disulfide formation sets in (101c). It is also possible to take the stand that esterification of the mercaptans by the sulfuric acid precedes the oxidation proper to disulfides, the ester formed breaking up into a disulfide and sulfur dioxide (59j), i.e.

$$(RS)_2SO_2 \rightarrow R_2S_2 + SO_2$$
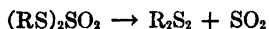
Another postulate calls for the formation of thiosulfonic esters, RSO_2SR (24b). Still another angle in oxidations with sulfuric acid is revealed in what seems to be trisulfide formation from free sulfur originating from hydrogen sulfide and sulfur dioxide liberated, a reaction surmised to be

$$2\ RSH + 2\ S \rightarrow R_2S_3 + H_2S$$
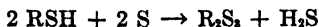
The trisulfides are credited with responsibility for the corrosiveness of naphthas (104).

Oxidations with nitric acid, though frequent, have not been studied in detail (109, 105, 98a, 51, 32, 29). Thus the possibility of nitration seems to have been largely overlooked, except in a case in which fuming nitric acid has been used on 2,4-di(methylmercapto)-1-ethylbenzene to produce the monosulfoxide of 5-nitro-2,4-di(methylmercapto)-1-ethylbenzene (85e). Again, as in the

case of urea types functioning like mercaptans, the presence of nitrous acid along with the nitric acid would make quite a difference (81a). In dealing with arylimidazole mercaptans, nitric acid is responsible for the removal of the—SH group altogether (106, 73). This reminds one of the same phenomenon when chromic acid is used jointly with sulfuric acid (107, 106). The combination of nitric and sulfuric acids yields polymers in addition to sulfonic acids (15), and there is no telling what aqua regia and the like may do. Mixtures of nitrogen oxides may be mild enough to yield sulfoxy compounds in some cases (98f, 98o), whereas nitrosyl chloride has been used gently to make disulfides (108, 96). But we have learned already that the latter also makes thionitrites (RSNO), which may be intermediates. One would also expect sulfuryl chloride to behave similarly if used mildly. More definite results may be expected with permanganate (109, 106, 91) and especially hydrogen peroxide (110, 85b, 16b), but very little has been done along those lines.

Disulfide formation in oxidation. If disulfide formation is an objective, one may even use copper sulfate (111, 23) or lead peroxide (98f, 15). Phosphorus oxychloride (112, 97b, 96), tellurium tetrachloride (113), etc., may function to some extent as oxidizing agents, and ferric chloride and ferricyanides serve the same purpose (114, 107, 97l, 97n, 53, 19a, 11, 10). This reveals a wide scope for inorganic oxidizing agents, quite a few of which have been made the subject of patents, since the odors of disulfides are not as objectionable in naphthas as are those of mercaptans.

Air is quite adequate in the production of disulfides from mercaptans (115, 98h, 5, 74a, 62, 62a, 57i, 57k, 52, 50, 33, 19,· 3). It is difficult to keep solutions of mercaptans in oil from oxidizing. This is particularly marked under alkaline conditions. On the whole, very little has been done in this field. When we consider that cysteine is oxidized to cystine by oxygen under biological conditions (74a) or in the presence or iron salts (114), and that there are other balances of the same type in the body, one might wish that much more had been done in this field.

The place of oxygen in disulfide formation can be taken by

ozone (116) or by electrolytic generation of oxygen (117, 62). The most famous equivalent, however, is sulfur (118). The well-known "doctor sweetening" of oils consists of converting mercaptans to lead mercaptides by reaction with alkaline plumbite solution. These are converted by free sulfur to disulfides and lead sulfide. Recently it has been shown that basic mercaptides are formed, and even peroxide derivatives, but that the final effect due to the addition of sulfur is either a slow or a rapid conversion to disulfides. We might suggest that biochemical research on similar reactions of compounds containing an —SH group involving oxygen may draw some inspiration from the work with sulfur. Reaction of mercaptans with sulfur has yielded disulfides.

Oxidations by halogens and halogen compounds. When we come to oxidations with halogens careful distinctions have to be made. Iodine seems to be the only one that can be relied on to yield disulfides only under alkaline conditions (119, 107, 106, 97g, 3). Bromine (120, 117, 97l, 85c, 78b, 59h, 57j, 48s, 31, 19a, 15, 5) and chlorine (121, 120c, 98h, 98s, 97m, 57j, 53, 15) are likely to yield sulfobromides and sulfochlorides under acid conditions and may lead to sulfoxides, sulfones and even sulfonic acids under alkaline conditions. In the case of some complex mercaptans which are very easily oxidized we are not certain that even iodine may not lead to sulfonic acid formation, and bromine has been known to split off the —SH group altogether when in excess, e.g. 1,4-acetamidonaphthyl mercaptan forms 4-bromo-1-acetylnaphthylamine (57j). Easily oxidized mercaptans, as *p*-phenylene dimercaptan, form polymeric disulfides first and substituted polymers subsequently (15). Commercial application has been made of this type of oxidation to "sweetening," or conversion to disulfides, by means of sodium hypochlorite solutions (121, 59j). This indicates that close control of conditions will segregate the various types of possible products, and where mixtures have been obtained consistency may yet be introduced.

Halogen-containing compounds such as sulfurylchloride (122, 120, 98o, 96, 53), thionyl chloride (123, 118a, 96), the sulfur chlorides (124, 123a, 118a, 92a), and even chloropicrin (125) exert an

oxidizing action in a variety of ways. The sulfur chlorides yield polysulfides, which are described as "not sweet" products. Tri-, tetra-, and penta-sulfides are on record. A distinction has been made between mercaptans on the basis of their reactions with sulfur monochloride (124c). A "real" mercaptan is one that reacts without liberation of sulfur; a "potential" mercaptan is one that reacts with liberation of sulfur. The distinction is illustrated thus:

$$2 \ CH_3CH_2SK + S_2Cl_2 \rightarrow (CH_3CH)_2S = S + 2 \ KCl \text{ (real mercaptan)}$$

$$2 \ (C_6H_5)C(=NH)(SK) + S_2Cl_2 \rightarrow S(C_6H_5C : NH)_2 + 2 \ KCl + 3 \ S$$
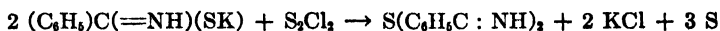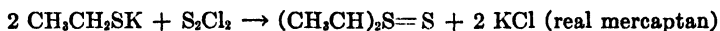
At the same time, it seems that if sufficiently diluted the monochloride may yield the disulfide. Thionyl chloride has been used for polysulfide formation. Sulfuryl chloride, however, yields disulfides mixed with sulfochlorides. In this instance, the sulfochlorides probably condense with mercaptan to form the disulfides:

$$RSH + R'SCl \rightarrow RS \cdot SR'$$
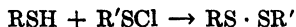
Chloropicrin normally produces disulfides, but it may also form compounds of the general formula $(RS)_3COR \ (SR)_3$ through loss of nitrous acid in the course of such oxidations.

Miscellaneous oxidations. Miscellaneous oxidation reactions abound. At times there are ring closures in complex cases (125a). We find diazobenzene chloride leading to disulfide formation (99). So may hydroxylamine (120), aryliminomethylenesulfoxylic acids (126), sulfinic acids (102b, 31), disulfoxides (123a, 31), formaldehyde sulfoxylate (126, 2) and chlorosulfonic acid (127, 59). This means that mercaptans are good reducing agents. They reduce, as a further instance, quinone to hydroquinone forming probably thio aldehydes (128). Even sulfur dioxide may act as an oxidizing agent with reference to mercaptans. In the presence of hydrogen chloride, sulfur dioxide may be used to make disulfides and even trisulfides (129, 123a). Polysulfide formation by oxidation with what we are accustomed not to consider as oxidizing agents may also be obtained with thionyl aniline, (C_6H_5NSO), and diethylaniline sulfide (130).

Many interesting problems arise in this field. When we note sporadic observations such as the formation of hydrogen peroxide in the autoxidation of mercaptans and the formation of peroxides by mercaptides (131), we feel that only a beginning has been made in the study of the oxidation of mercaptans. Even though we have but little as yet upon which to found analogies with phenols and alcohols, the possibility is being opened up (132, 130, 118d, 117, 98e, 30a, 28).

5. Miscellaneous reactions

Mercaptans react with alkyl magnesium halides to produce alkylmercapto magnesium halides and hydrocarbons (133). This is in line with the analogous behavior of alcohols in Grignard condensations. Ethyl mercaptan, ethyl magnesium bromide and benzoyl chloride yield ethyl thiobenzoate; if ethyl chloroformate is used, ethyl thiocarbonate is obtained (133a). Synthetic building up of mercaptans may be accomplished as in the case of alcohols.

Substitution of $-SH$ hydrogen together with substitution in the ring takes place when aromatic mercaptans are treated with chlorine in chloroform or carbon tetrachloride (120c, 98h, 34). There may be simultaneous oxidation to halogen-substituted disulfides. We have already remarked that excess halogen may cause the entire loss of the $-SH$ group in complex mercaptans (98h). Somewhat puzzling then, is the reported formation of ethyl bromide from ethyl mercaptan and bromine (19b). It is quite to be expected however, in the case of the curious mercapto-silicon chloride, $SiCl_3SH$, which gives $SiCl_3Br$ (196).

A "Gabriel" reaction (134, 120a, 101b), amounting to the conversion of one mercaptan to another, is illustrated by the case of the reaction of N-(γ-mercaptopropyl)-phthalimide with fuming HCl in a bomb tube:

$$C_6H_4 \underset{CO}{\overset{CO}{\diagdown \diagup}} N(CH_2)_3SH \rightarrow C_6H_4(COOH)_2 + HSCH_2CH_2CH_2NH_2$$
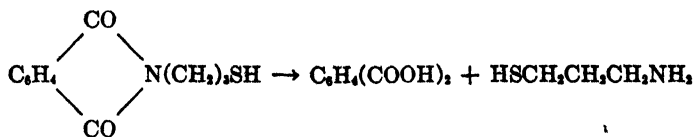
Mercaptoamines are thus formed. This parallels aminoalcohol formation.

Stress should be laid on the observed substitution of —SH groups, not only because of the apparent analogy with alcohol chemistry, but also because of the similarity to reactions in which an —SH group is hydrolyzed off, as it were, with the formation of hydrogen sulfide (135, 120c, 57, 53, 9, 3). Thus the same $SiCl_3SH$ on treatment with alcohol yields hydrogen sulfide (19b), while triphenylmethyl mercaptan loses hydrogen sulfide on treatment with cold concentrated sulfuric acid, boiling acetic anhydride, dilute alkali, sodium ethoxide or even alcoholic silver nitrate (53). The last reaction shows an analogy with alkali hydrosulfides, since silver sulfide is formed. Removal of —SH groups by similar mechanisms is possible with alcoholic ammonia or potassium hydroxide at elevated temperatures in some exceptional types, as, for example,

$$p\text{-}CH_3 \cdot C_6H_4CO \cdot CH : C \underset{SH}{\overset{SH}{<}} \tag{9}$$
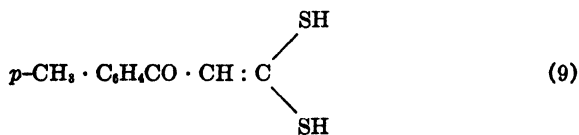
Simple hydrolysis with water alone at elevated temperatures has also been reported, at least for ethyl mercaptan.

A claim has been made that mercaptides react with disulfides (97f) in a kind of rearrangement:

$$R'SSR' + 2 R''SK \rightarrow 2 R'SK + R''SSR'$$
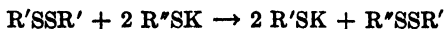
Such shifts may not be uncommon. Another phenomenon which has received practically no attention is the possible polymerization of mercaptans (74b).

A rather unusual reaction, too, is the reduction of substituted persulfides (RSSH) to simpler mercaptans (RSH) by sodium arsenite or potassium cyanide (136).

A large variety of analogies may be suggested for research. These would be parallel to pinacoline transformations, such as the transformation of di-primary, primary-secondary, primary-tertiary and di-tertiary dimercaptans to thio ketones. One might

parallel the dehydration of aromatic alcohols mixed with aromatic hydrocarbons, e.g. the reaction of benzyl mercaptan and benzene in the presence of sulfuric and acetic acids to form diphenylmethane, or the similar reaction to synthesize triphenylmethane. There should be analogues of the condensations with the "methane carbon atom," such as that of phenol, oxalic and sulfuric acids to form aurin $(HOC_6H_4)_2C=C_6H_4=0$. Condensations of anthrol derivatives suggest numerous possibilities in the dye field. Some of the simpler reactions need investigation, as, for instance, the formation of the analogue of resorcin green, which is formed by the action of nitrous acid on resorcinol, or the formation of dinaphthols by the action of ferric chloride on the naphthols. One may expect a material increase of our knowledge contributory to analytical detection and to practical utilization.

To augment our list of reactions, untouched or practically untouched, we may mention possibilities that suggest themselves in the reduction of phenol to hexahydrophenol, oxidation of side chains of phenols, reduction of hydroxy acids by hydrogen iodide, direct replacement of groups, as Cl or $-NH_2$, by $-OH$, Skraup's synthesis, Kolbe and Schmitt syntheses, and syntheses of hydroxy acids, as illustrative of a host of not only analogies, but also contrasts.

III. METHODS OF PREPARATION AND PURIFICATION

1. Occurrence and isolation from natural products

Methyl mercaptan has been reported in numerous biological sources, in fresh roots as well as in decomposing organic matter (137). Ethyl and isoamyl mercaptans seem to be normal by-products in the metabolism of yeast or micro-organisms (138). The reason why other homologues have not been reported lies probably in the qualitative way in which the matter has been approached. If we include thio acids, sulfur-containing amino acids as cysteine, glutathione, in our list, the $-SH$ group becomes almost omnipresent (139). Coagulated egg white gives the nitroprusside test (139c). A thio sugar of known constitution has been found in yeast. It is even stated that insulin's physiological

activity depends on the sulfur part of the molecule. If we consider the multiplicity of reactions possible in the decomposition of these more complex compounds containing —SH groups and the patent fact that simpler mercaptans do form readily in the metabolism of such foods as asparagus or spinach (137b, 137c), it is not surprising that petroleum, its distillates, shale oils and coal tar distillates are good sources of mercaptans, since they ultimately originate from living matter.
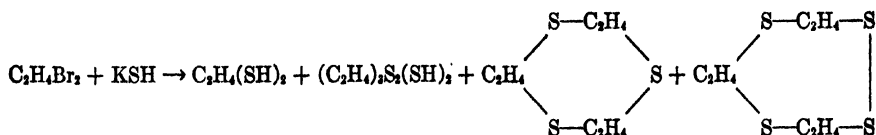
The isolation of mercaptans from natural sources, if it be merely a matter of scientific interest, can be accomplished by a judicious choice of reactions. Industrially, aqueous caustic soda is employed to remove the lower aliphatic mercaptans and some thiophenol, and hence these washings may serve as a limited source of of these mercaptans. Mercaptans can also be recovered from refinery acid sludges in which they dissolve as such, especially at lower temperatures. Quantitative separations in the form of mercury derivatives and the like, are, of course, possible, even if they are not practised.

2. Synthetic methods

Direct introduction of — SH group by substitution. The most obvious approach in the synthesis of mercaptans is the substitution of an inorganic radical already present in an organic compound by an —SH group from an inorganic source, such as hydrogen sulfide, a sulfide, or a hydrosulfide. The simplest case reported recently is the formation of ethyl mercaptan from ethyl iodide and aqueous hydrogen sulfide (140). This takes place even in acid solution and is accelerated by the presence of precipitated sulfides or other adsorbing agents. Rather unexpected is the reaction of hydrogen sulfide with silicon tetrachloride leading to the formation of $SiCl_3SH$ (19b). Apparently one might expect analogies to appear in the inorganic field as well.

Reactions with hydrosulfides have been practised on the most varied types of halogenated compounds even to the extent of determining the orientation of entering —SH groups (141, 132a, 114b, 105f, 98u, 78b, 74b, 57d, 53, 51, 29, 27, 19). Thio acids

(141p, 119e, 119f, 111, 57i), thio sugars (141c, 141r, 141s, 141t), thiopurine derivatives and the like (141b, 141e, 141m, 110b, 98l, 98q, 57g, 33), have been made by such procedures. We should like to point out that it is often overlooked that there may be other products formed, as, for instance, dithio acids in the thio acid syntheses. It is also possible to get polysulfides, as, for instance, triethylene disulfide dimercaptan and more complex compounds in the reaction of ethylene bromide with KSH (115d), thus

$$C_2H_4Br_2 + KSH \rightarrow C_2H_4(SH)_2 + (C_2H_4)_2S_2(SH)_2 + C_2H_4 \begin{array}{c} S{-}C_2H_4 \\ \diagup \qquad \diagdown \\ \qquad\qquad S + C_2H_4 \\ \diagdown \qquad \diagup \\ S{-}C_2H_4 \end{array} \begin{array}{c} S{-}C_2H_4{-}S \\ \diagup \qquad\qquad | \\ \qquad\qquad | \\ \diagdown \qquad\qquad | \\ S{-}C_2H_4{-}S \end{array}$$

Variants on direct use of hydrosulfide. The conditions are often varied, sodium sulfide being used instead of the hydrosulfide; nor is it necessary to work with a halogen derivative (142, 141g). Thus, analogously to the potash fusion of sodium benzenesulfonate to obtain phenol, one may get a small yield of thiophenol by the use of potassium hydrosulfide. A general method has been reported whereby alcohols are treated with red phosphorus, moist sodium sulfate and sodium sulfide, and bromine (143). This is essentially a modification of the above procedures, with the curious fact that the sodium sulfate is a source of sodium sulfide or hydrogen sulfide:

$$6\ ROH + 3\ Br_2 + 2\ P \rightarrow 6\ RBr + 2\ P(OH)_3$$

$$4\ P(OH)_3 + Na_2SO_4 \rightarrow Na_2S + 4\ H_3PO_4$$

$$Na_2S + H_3PO_4 \rightarrow Na_2HPO_4 + H_2S$$

$$RBr + H_2S \rightarrow RSH + HBr$$
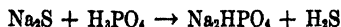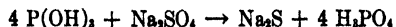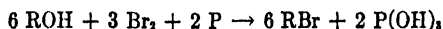
The yields are good.

In the same class we may put reactions whereby an $-NH_2$ group is replaced by $-SH$ by diazotizing and treating with an alcoholic sulfide or hydrosulfide to liberate nitrogen. Better yields are obtained if the diazotized compound is first treated with a xanthate or a thiosulfate and then hydrolyzed. In some cases the use of xanthates to react with the halogen derivative

can be made direct.   On hydrolysis the mercaptan structure is opened up (144, 141k, 98s, 92a, 8).

Addition of hydrogen sulfide to unsaturated compounds, and reactions with alcohols and the like.   Before we go on with cases of this sort we stop to consider the cases in which hydrogen sulfide has been used to add to unsaturated compounds.   Strangely enough, direct addition to olefins has not been investigated, although ethyl mercaptan is mentioned as a by-product in the reaction of acetylene with hydrogen sulfide at 425–50° (145).   Indirectly this is accomplished when alcohols are passed over thorium dioxide with hydrogen sulfide at temperatures at which olefins may form (146, 58).   There is also reason to believe that alcohols may be sufficiently dehydrated by concentrated sulfuric acid to react with hydrogen sulfide to form mercaptans, at least of the aliphatic series (41).   In the case of sugars the —SH group may be introduced by means of hydrogen sulfide in the presence of pyridine (141i, 141s, 84, 42).   Furthermore, esters may be simultaneously hydrolyzed and caused to react with hydrogen sulfide to form mercaptans (87).   A very interesting case of a more complex nature is the conversion of the corresponding —OH compounds to the carbothiols of malachite green and of crystal violet merely by the action of hydrogen sulfide (13a).   We also think it proper to surmise that the formation of mercaptans in fermentation may be due to the reaction of alcohols with hydrogen sulfide.   It may not be safe to speculate that wherever water adds to yield hydroxy compounds, hydrogen sulfide will add to yield mercaptans, yet we can cite cases in which such similarities are well indicated.   Benzalacetophenone will add hydrogen sulfide to form a sulfhydrin (147); with favorable structures a —C=N— group will add hydrogen sulfide to form a mercapto compound (125a), and the like.

It is but a small transition from the above to cases where phosphorus sulfides have been made to react with hydroxy compounds (148), such as phenols (141m, 132b), carbostyril (16b), hydroxyquinaldine (16b), and benzohydrol (148a), to form the corresponding thiols.   Aluminium sulfide and hydrated sodium sulfate (57) constitute a reagent somewhat analogous to that

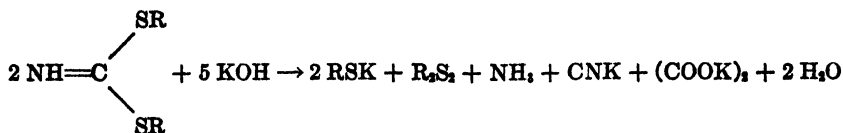acting in the instances in which hydrogen sulfide reacts as it is formed.

By various hydrolyses. Very numerous are the cases in which the mercaptans are obtained finally by the hydrolysis of some compound which may itself be a synthetic mercaptan. We have mentioned the Gabriel reaction for aminomercaptans, but it need not be restricted to this type and is applicable to the formation of dimercaptans (134, 120a, 101b, 86, 72, 3). Xanthates and xanthic acids can be hydrolyzed to mercaptans or mercapto acids (149, 144, 144a, 144b, 144c, 141f, 119f, 98s, 93, 8). Hydrolysis of mercapturic acids gives cysteins (137g, 74a). Hydrolysis of cystine derivatives yields mercaptans (150). Many thioglycols have been made by the hydrolysis of thiourethans (14). Thus,

$$NH_2 \cdot CS \cdot S(CH_2)_nS \cdot C : S \cdot NH_2 + 4 \ KOH \rightarrow 2 \ KSCN + KS(CH_2)_nSK.$$
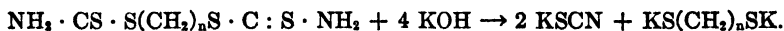
Ring closures may occur (151, 120a, 106, 97g, 12, 10), such as when acetylallylarylthioureas on refluxing with dilute hydrochloric acid yield arylimidazole mercaptans (73). Rings are opened up also, as when diphenylthiohydantoin yields on hydrolysis thioglycolic acid (152).

Hydrolysis of β-ethylmercapto-crotonic acid ethyl ester favors preferentially the splitting off of a mercaptan (100a). In the case of a compound like $C_6H_4(NO_2)(CHSCONH_2)$ (156), hydrolysis leads to the formation of a mercaptan. We may mention as sources of mercaptans such compounds as CCl_3—$C(SCH_3)$ $(NH \cdot HCl)$ (76), mercaptotriarylcarbonium salts (153), esters of thio acids (96), the addition compound of dimethyl sulfate with thiourea (154), and thiourea derivatives (154a, 107, 21a), phenylthiomethyl acetate (98f), phenylsulfoxyacetic acid (155), thio esters of thiophthalic acid (141o), the diacetone compound of 3-thioglucose and the like (158, 141c, 141s, 141t, 132j, 84a), thiourethan glycoside (14), mercaptals (84), ethyl trithiocarbonic acid (144), and types like $(C_6H_5S)_2C(CH_3)(CH_2COOC_2H_5)$ (78). Add to this heterogeneous group the hydrolysis of Grignard reagents containing sulfur, usually made by the use of free sulfur, to obtain quite a variety of mercaptans (157, 141, 133, 117,

30, 30a, 25). A very general equation, representing hydrolysis of thiosulfocarbamates (6), is expressed by

$$2\ NH{=}C{\bigg\langle}{\begin{matrix} SR \\ \\ SR \end{matrix}} + 5\ KOH \rightarrow 2\ RSK + R_2S_2 + NH_3 + CNK + (COOK)_2 + 2\ H_2O$$

and still another involving thio acid esters (6):

$$NH_4CS \cdot SR \rightarrow NCSH + HSR$$
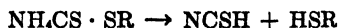
Rather unusual are conversions of thiocyanates to mercaptans by concentrated sulfuric acid (159,1). Dimethyl sulfate in very exceptional cases can be made to remove an —SH group from a compound to form methyl mercaptan (125a). The group —SCOC$_6$H$_5$ can be converted to an —SH group by ordinary hydrolysis when appearing in ring compounds (156).

There remain also a few cases where drastic action which may be considered as hydrolysis leads to mercaptan formation. Such is the formation of o-thiocresol from thionaphthene (160) and the decomposition of disulfides to mercaptans and sulfonic acids along with other products by caustic potash (161, 124e, 102b). More complex variants will not be discussed here (162).

By reductions. Quite as important are numerous cases in which mercaptans have been synthesized by reducing some other compound. The disulfides, if available, are very convenient (163, 146b, 138d, 117, 114b, 101, 97, 97m, 82j, 57m, 9c, 8c, 6). As reducing agents we find alkali sulfides (136, 132i, 124e, 100b, 31, 19a), glucose in alkali (163, 97n, 82b), zinc dust in alkali or acid (161b, 123a, 115b, 98r, 97j, 35, 15), active aluminium (163a, 163i), sodium (163d, 97i, 97j, 82h), tin and acid (82b), electrolysis at the cathode (114a), the Grignard reagent (30), mercury with or without chloroform (163b), and mercaptides themselves (97f). It is doubtful whether sulfides as a class are reducible by such means to mercaptans, yet exceptions seem to exist in the case of o-nitrophenyl sulfide and sulfides of the type C$_6$H$_5$CH$_2$—SCH$_2$COR (164). In the latter cases benzyl mercaptan has been obtained by reduction with sodium, zinc and acid, and even hy-

droxylamine hydrochloride (97j). We are not prepared to say whether these are really exceptions, since the field has not been widely investigated. The reduction of tri- and tetra-sulfides to mercaptans, which takes place with the same reagents as the disulfides, is more easily understood (123a, 82h).

Other compounds that are reducible to mercaptans are sulfonic acids (165, 121a), thiosulfonic acids and their esters (165, 161c), and sulfochlorides derived from sulfonic acids (166, 157b, 119c, 115, 114c, 102c, 100, 100c, 98e, 98h, 97, 97e, 85c, 85d, 85e, 67, 59i, 57j, 57k, 34, 32, 11) either under acid conditions with metals or by electrolysis (167, 117, 115c, 114a). Sulfonamides may be reduced by hydrogen iodide and phosphorus (168). This list may be expanded to include sulfoxides (169, 161c, 115b, 105b, 99a, 31), sulfinic acids (170, 119c, 115b, 82g, 16) and sulfenic acids (171) and their derivatives, alkyl hyposulfites (172, 132e) and thiocyanates (159a, 100g, 19), sulfoxylates (2) and sulfanilides (167b). Of some special interest is the reduction by aniline of compounds of the type RSCCl₃, where R is an aromatic radical, to mercaptans of the aromatic series with the formation of triphenylguanidine as a by-product (173, 132g). Little explored has been the reduction of ring compounds containing sulfur to mercaptans. Thus from a knowledge that thionaphthene is reducible to o-ethylthiophenol (174), or that toluylene diazosulfide
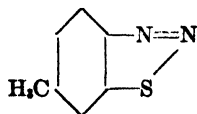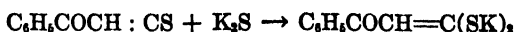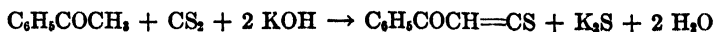

is reducible to 1-methyl-4-amino-3-mercaptobenzene (175)

we can visualize many possibilities of the similar opening up of sulfur-containing rings.

By reaction with sulfur. Reaction with sulfur may serve as a means of forming mercaptans. Sulfur reacts with benzene in the

presence of aluminium chloride to form phenyl mercaptan (176, 118e). It reacts similarly with phenylhydrazine (177), diphenylamine (178), and aminodiphenylamine (178). The reaction of sulfur with hydrocarbons unquestionably yields mercaptans, but the matter has been taken up only very qualitatively, and, to judge from the number of cases in which they have not even been looked for, rather carelessly.

By thermal or similar decomposition. A few instances are available in which thermal or similar decomposition by scission serves as a source of mercaptans. These might have a very important bearing on the frequently observed evolution of hydrogen sulfide and mercaptan formation on heating crude petroleum or its fractions whether they have been refined or not. Mercaptides, sulfides and disulfides are definite sources of mercaptans (179, 124d, 98c, 77, 57c, 57f, 32a, 7). Sulfonic and thiosulfonic acids and their derivatives, sulfoxides, sulfocyanacetic esters, and iminothiocarbonic esters, $(RS)_2C:NH$, have also been mentioned (182, 162f, 162h, 155, 115a, 78, 59f, 6).. In a theoretical fashion derivatives of thiourea and xanthates have been studied (180, 162e, 151c, 149, 81a, 28, 6). Observations of mercaptan evolution have been made occasionally in attempts to distill complex sulfur compounds (181, 148c, 128a, 971, 77). In these cases there seems to have been established a definite tendency for alkylmercapto groups to be split off on heating as component parts of simple mercaptans provided a hydrogen atom is available. Simple fundamental investigations are conspicuously absent.

By condensation. Condensations may be called upon in mercaptan syntheses. An interesting type is represented in the formation of phenyl β,β-dimercaptovinyl ketone from acetophenone and carbon disulfide (97c, 9), thus

$$C_6H_5COCH_3 + CS_2 + 2\ KOH \rightarrow C_6H_5COCH{=}CS + K_2S + 2\ H_2O$$

$$C_6H_5COCH : CS + K_2S \rightarrow C_6H_5COCH{=}C(SK)_2$$

Similar condensations are possible with acetone dicarbonic acid ester, hydroxyquinoline derivatives (183), sulfocarbazinic acids $(RNH\cdot NH\cdot CS\cdot SH)$ (57a), ketones like α-thienyl methyl ke-

tone (9). Xanthates may be used in these reactions, which serve also as a basis for synthesizing mercaptothiazolines. Thiurets and alkyl iodide addition compounds of urea with primary and secondary amines furnish mercaptans (184). We find a few instances of direct condensation with carbon disulfide. Thus, potassium azide reacts to form potassium azidodithiocarbamate, $KS \cdot C(:S) \cdot N_3$, which has a mercaptan structure (57e). The general reaction $RHgOH + CS_2 \rightarrow RHgSH + COS$ has also been noted (180a). The substances $RHgSH$ may be considered as mercaptans. Mercaptothiazoline formation (151b, 120a, 97g) may also be illustrated simply for the case of 4-methyl-2-mercaptothiazoline from propylenimine, thus
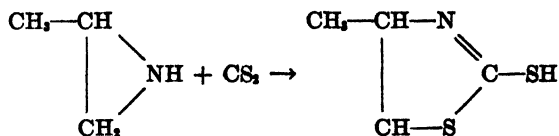
Ring closure, too, is thus illustrated (151, 151a, 151b, 151d, 151e, 106, 97g, 10). More attention, too, should be paid to the relatively easily carried out reaction between hydrogen sulfide and formaldehyde (185) which is said to result in the interesting stable substance, methylene mercaptan, $CH_2(SH)_2$. This is in striking contrast with the instability of two —OH groups on the same carbon atom. On the other hand, we may remark here, all efforts to make NH_2SH have failed (186). Amongst the curiosities are also the "thioprussiamic acids" (187), obtained by the reaction of thiourea with ammonium thiocyanate, for example,

$$(NH_4)_2 : (CN)_3 \cdot NH \cdot (CN)_3 (NH_2) (SH)$$
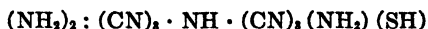
Another type which is receiving a little attention is that represented by the formula RCSSH, dithio acids or carbithionic acids (161a, 136). They may be made from aldehydes and hydrogen persulfide directly (141q), e.g.

$$C_6H_5CHO + H_2S_2 \rightarrow C_6H_5CSSH + H_2O$$

and are stronger acids, as a rule, than acetic acid. Alternative approaches are to be found in the production of dithioformic

acid from chloroform and potassium sulfide (141p), or the forma-
tion of C_2H_5SSH by reducing sodium ethyl thiosulfate with
potassium sulfide (136).   These dithio acids may serve as sources
of simple mercaptans, since they may be reduced by such reagents
as potassium cyanide or sodium arsenite (136).

It is apparent that the scope of synthetic methods may be
expanded a great deal by paying closer heed to suggestions from
oxygen chemistry.   Analogies should be attempted, for instance,
to aldol condensations and the Cannizzaro reaction, and to vari-
ous means employed for reducing aldehydes, ketones, and quin-
ones to alcohols, glycols and phenols.   Thio aldehydes should
add hydrogen cyanide, and then become convertible to thio
acids.   To mention but a few prospects, it should be possible to
prepare mercaptocitric acid, to parallel the closure of phenyl-
isocrotonic acid to α-naphthol, to prepare thiopinacones, or to
obtain exact analogies of the two types of hydrolysis of aceto-
acetic ester.   But, perhaps, most important of all would be a
re-examination of the old data with a view toward making them
more valuable from both the practical and the scientific view-
points.

IV. DETECTION AND DETERMINATION

A few color tests are described, none of which, however, has
been elaborated.   The reaction of nitrosylmercaptides with nas-
cent nitrous acid is said to distinguish primary and secondary
aliphatic mercaptans by the formation of a red color (188).
Tertiary and aromatic mercaptans as well as thio acids give a
green color turning to red.   For triphenylmethyl mercaptan a
sensitivity of 1:7500 is given.   Ethyl nitrite or N_2O_4 also give
red colors (189).   Chloropicrin, bromopicrin and tetranitrome-
thane (190) have been used to distinguish between ethyl mercap-
tan and ethyl sulfide, but not too successfully.   There is also
much to be desired in the study of color changes on the addition
of concentrated sulfuric acid (150, 9).   All we can say is that
they are many,—the usual gamut being from green to blue.   A
similar situation exists with tests with ferric salts (191, 141h,
141j, 119f).   Mercaptans proper and thio acids should yield
deep reds, yet α-mercaptocinnamic acid gives a deep green (191).

Identification by derivatives has fared considerably better. Many mercaptides (192, 102a) have been described, as well as mercaptals, mercaptoles (192h), and the like. 3-Nitrophthalic anhydride has been strongly recommended for this purpose (193).

Some efforts have been made to develop alkalimetric titration of aliphatic mercapto acids (194). If one has favorable conditions there are available titration methods with iodine and alkali (195, 44a), permanganate (52), or silver nitrate with ammonium thiocyanate (196). If only mercaptans are present, lamp sulfur determination may be made if no great accuracy is required (57n). A method not sufficiently well-known is one based on the reaction of a mercaptan with methyl magnesium iodide (197). Methane is formed and its volume is measured:

$$RSH + CH_3MgI \rightarrow CH_4 + RSMgI$$
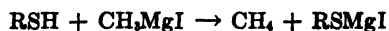
The chief weakness of all the methods reported here is that they require particularly suitable conditions for their execution, and that they have not been tried on a sufficient variety of mercaptans.

We may add for completeness that it is possible that mercaptans may be of use as analytical reagents. A hint to that effect is to be found in the fact that thioacetamide may be used as a reagent for arsonic acids (198). From a knowledge of the characteristics of mercaptals and mercaptoles, mercaptans may serve as reagents for detecting and determining aldehydes and ketones (192h). In fact many reactions of mercaptans may be so adapted.

V. SPECIAL INTERESTS ATTACHING TO MERCAPTANS

We have mentioned the special interest that attaches to the study of the behavior of the —SH group in biological chemistry. The physiological effects, which may be serious, have been amply described (199). Severe irritations may occur from contact with liquid mercaptans, whereas vapors cause giddiness and headache. A remarkable effect on the eyes is the involuntary drooping of the lids accompanied by a protracted sensitivity to light. And yet mercaptans have been reported in the skin itself! Metabolic experiments are being multiplied, but the acme of interest lies in the regulative action in cell metabolism of compounds con-

taining mercapto groups, particularly reduced glutathione, cysteine and thioglycolic acid, when present in equilibrium with the disulfide forms (200, 137d). Additive compounds of the two forms have been postulated, peroxide formation has been asserted and denied, and the nature of the oxidations that go on has been studied from the point of view of autocatalysis. We cannot review the mass of data which is being accumulated, mostly because of its chaotic condition, but we would point out that the —SH group has been involved in discussions of topics from the fertilization by spermatazoa to the cure of cancer.

An outgrowth of such interest is the application of mercapto compounds to therapeutic uses (201) and even to synthetic food problems (202, 163h). Amino metal mercapto compounds, such as the sodium salt of 4-acetylamino-2-argentomercaptobenzene-1-carboxylic acid, are useful in spirochete infections. Metal mercapto acid esters are also used. The addition compound of α-furfuryl mercaptan with the Grignard reagent has been used to synthesize derivatives showing vesicant action (35). We have already mentioned the well-known syntheses of soporifics from mercaptals and mercaptoles. Therapeutic use has been made also of the metallic compounds of thioglucose (203). Quite engaging, too, is the discovery that furfuryl mercaptan and α-hydroxymethylfurfuryl mercaptan and their disulfides make a synthetic coffee aroma (202).

In synthetic work a varied use of mercaptans may be found. Optically active amyl mercaptan has been used for racemic splitting of sugars (204). The greatest use of mercaptans, of course, has been as intermediates in the synthesis of dyes, particularly vat dyes. Thus, the anthraquinone series has been pretty well covered and thioindigos are derived from thio acids (205). Amino thiophenol serves as the starting point for indamine colors (206). Of some importance is the observation of the bathochromic action of the methylmercapto group in azo dyes (206). To deepen shades it is, therefore, often desirable to obtain a mercaptan and methylate it. The rubber field as well claims efforts in the direction of synthetic mercapto compounds (207). The mercaptobenzothiazoles stand out in importance, but it is highly probable that others will be found.

A vast field for the production and conversion of mercaptans is to be found in petroleum technology. If all the mercaptans present in unrefined naphthas in this country were to be recovered there would be available, conservatively, from 150 to 200 tons of mercaptans per day. Many a process could be evolved for their utilization if more attention were paid to the fundamental chemistry of at least the relatively simpler ones found in petroleum. One would go far beyond such applications as mingling mercaptans with illuminating gas (about ten pounds per million cubic feet) to detect leaks and the like (208). It is rather surprising that of scores of patents for "sweetening" oils, almost all deal with the conversion of mercaptans to disulfides and not their removal (210, 209, 118, 54). Caustic washing removes completely only methyl and ethyl mercaptans. As for the rest they travel on to be consumed in gasoline or to be treated out by wasteful chemical means.

We should like to close our review with the prediction that we are only at the threshold of a renaissance of interest in mercaptan chemistry.

VI. CONDENSED LIST OF SUGGESTED RESEARCH PROBLEMS

1. A critical examination and determination of fundamental physical constants of representative mercaptans.

2. Studies on physical state, association, light absorption and scattering, etc.

3. Thermodynamic data on a selected series.

4. Physical studies on conductivity, dielectric behavior and ionization.

5. Study of hydrate and addition compound formation.

6. Adsorption on surfaces.

7. Distribution between solvents.

8. A detailed investigation of thermal decomposition.

9. Decomposition by physical agencies other than thermal.

10. Comparative study of principal reactions, such as esterification, of alcohols, phenols and mercaptans from a physicochemical point of view.

11. Quantitative investigation of mercaptan-disulfide equilibria in oxidation-reduction systems.

12. The autoxidation of mercaptans and peroxide formation.

13. An investigation of the mechanism of decomposition reactions which lead directly to the formation of mercaptans.

14. Study on orientation of substituting groups in aromatic mercaptan types and the like to determine relative influences.

15. Development of analytical methods with a view toward extending them and rendering them more useful in research.

16. Development of methods for the complete extraction and fractionation of mercaptans from commercial sources.

17. Utilization of commercially extracted mercaptan mixtures.

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